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THE MASS-YIELD CURVE FOR FISSION OF NATURAL URANIUM BY 14-MeV NEUTRONS

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(*Received* 21 *January* 1957)

Abstract—Relative yields for the fission of natural uranium (effectively ^{238}U fission) by 14-MeV neutrons have been measured for mass numbers 89, 91, 99, 111, 115, 140, 143, 144, 147, 153, and 156, and the general shape of the mass-yield curve is given. The peak-to-trough ratio is 9·1; the average number of prompt neutrons emitted per fission is found to be (4 ± 0·5); and a value for the absolute fission yield of ^{99}Mo is found to be (5·58 ± 0·56) per cent. The light peak has moved 3–4 units towards the heavy peak when compared with the 14-MeV fission of ^{235}U.

A CONSIDERABLE number of mass-yield curves have previously been published for natural uranium. Most of the work on thermal fission yields in ^{235}U has been carried out on it, as has pile fast-neutron fission work (effectively ^{238}U fission).[1,2] Fission yields of natural uranium have also been measured for photofission by 16-MeV γ rays.[3] As far as fission by 14-MeV neutrons is concerned, the only published work is on ^{235}U.[4,5,6,7]

In general, as the energy of the fissioning particle increases, the probability of fission by the less probable modes increases, i.e. the trough in the mass-yield curve fills up, the peaks are lowered, while the wings tend to splay out slightly.

This paper gives the relative fission yields for eleven mass chains for 14-MeV fission of natural uranium. The results are sufficient to show the general shape of the curve and to make a rough estimate of the number of prompt fission neutrons, but not to show the presence of fine structure. (Since fission cross-sections for uranium isotopes for high-energy fission may be expected to be of the same order of magnitude, the effect of the ^{235}U may be ignored and the experiments considered to be effectively the fission of ^{238}U.)

EXPERIMENTAL

Irradiations

The targets used for the determinations weighed approximately 40 g and were made from uranium metal, in the form of a cylinder with a large well machined in the centre. This target fitted over the end of the target tube of the Cockcroft-Walton accelerator and were irradiated with 14-MeV neutrons produced by the (d,T) reaction. The neutron flux at the target was checked for the presence of thermal neutrons produced by scattering from nearby structures, but the effect was found to be negligible.

* Present address: Argonne National Laboratory, Lemont, Illinois, U.S.A.

[1] D. W. ENGELKEMEIR, J. A. SEILER, E. P. STEINBERG, and L. WINSBERG *National Nuclear Energy Series* Vol. 9B. Paper 218. McGraw-Hill, New York (1951).
[2] R. N. KELLER, E. P. STEINBERG, and L. E. GLENDENIN *Phys. Rev.* **94**, 969 (1954).
[3] H. G. RICHTER and C. D. CORYELL *Phys. Rev.* **95**, 1550 (1954).
[4] R. W. SPENCE *U.S.A.E.C. Report* A.E.C.D. 2625 (1949).
[5] J. TERRELL, W. E. SCOTT, J. S. GILMORE, and C. O. MINKINNEN *Phys. Rev.* **92**, 1091 (1953).
[6] A. C. WAHL and N. A. BONNER *Phys. Rev.* **85**, 570 (1952).
[7] A. C. WAHL *Phys. Rev.* **99**, 730 (1955).

The irradiation periods were of the order of 4 hr, during which time the flux remained substantially constant.

Chemical Separations

Solutions of carriers of strontium, yttrium, molybdenum, silver, cadmium, barium, cerium, praseodymium, neodymium, samarium, and europium were placed in a flask with the target, and a reflux condenser connected. Dissolving was carried out using hot nitric acid in the presence of a stream of oxygen and with 3 N nitric acid trickling down the condenser. The acidity in the dissolving vessel was ~8 N at the start of dissolving and ~3 N at the end.

The uranium was removed from the target solution by extraction with a 20 per cent vol./vol. solution of tributyl phosphate in kerosene. Six successive equal volume extractions were required to remove virtually all the uranium.

After extraction of the uranium, the carrier solution was evaporated nearly to dryness, neutralized, and treated according to the separation procedure of COOK and CROUCH.[8] Briefly, this consists of fusing with a mixture of KOH, K_2CO_3, and KNO_3 and leaching out molybdenum (and ruthenium if present) from the cooled melt with water. The residue is then fumed with HNO_3, HF, and $HClO_4$ and the final residue dissolved in water. Rare earths, yttrium (and zirconium if present) are then precipitated with ammonia, silver with HCl, cadmium with H_2S, and barium and strontium with carbonate. Having separated the elements, they were purified by standard radiochemical purification procedures based on those of MEINKE,[9] with the exception that rare earths and yttrium were separated by lactic acid elution from a Zeokarb-225 cation exchange column.[10,11] The radiochemical purity of every source was checked by following the decay of the sources. This was continued for 5 half-lives or for 6 months, whichever was the shorter.

Counting Procedure

The purified sources were filtered by a filter-stick technique which gives very smooth, even precipitates, and the filter papers mounted on a thick aluminium tray. The sources were 1·6 cm in diameter and usually weighed about 20 mg. Chemical yields were obtained by direct weighing.

The counter used was a standard 2π-β-proportional flow counter, using methane as the counting gas. Corrections were applied for self-absorption, self-scattering, and back-scattering from source and tray, and for conversion electrons, growth of daughter nuclides, and other genetic phenomena. The details of these counting corrections have been recorded by CUNINGHAME, SIZELAND, and WILLIS.[12]

Calculations

All calculations of saturation activities were made using the normal growth and decay relationships, full allowance being made for genetic corrections where these were applicable. In the case of nuclides where the parent was of comparable half-life to the irradiation time (i.e. ^{91}Y, ^{143}Pr, and ^{156}Eu) the following expression was used to calculate the saturation activity:

$$A_s = A_0/f$$

where A_s = saturation activity, A_0 = observed activity at time t, and

$$f = \frac{\lambda_2}{\lambda_2 - \lambda_1}\left[e^{-\lambda_1 T}(1 - e^{-\lambda_1 T}) - e^{-\lambda_2 T}(1 - e^{-\lambda_2 T})\right] + e^{-\lambda_2 t}(1 - e^{-\lambda_2 t})$$

where λ_1 and λ_2 are the parent and daughter decay constants respectively, t is the time elapsed between the end of the irradiation and separation of parent and daughter, and T is the irradiation time.

The standard deviations quoted in the results were calculated for each nuclide after giving due allowance for all possible errors. In the case of ^{143}Ce an additional allowance was made for the fact

[8] E. A. C. CROUCH and G. B. COOK *J. inorg. nucl. Chem.* **2**, 223 (1956).
[9] W. W. MEINKE *U.S.A.E.C. Report* A.E.C.D. 2738 (1949).
[10] J. G. CUNINGHAME, M. L. SIZELAND, H. H. WILLIS, J. EAKINS, and E. R. MERCER *J. inorg. nucl. Chem.* **1**, 163 (1955).
[11] E. C. FREILING and L. R. BUNNEY *J. Amer. chem. Soc.* **76**, 1021 (1954).
[12] J. G. CUNINGHAME, (Miss) M. L. SIZELAND, and H. H. WILLIS *U.K.A.E.A. Report* A.E.R.E. C/R 1646 (1955).

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that only one determination was made. In all other cases at least two, and usually three, other determinations were made.

RESULTS

Table 1 shows the results of the fission yield determinations and Fig. 1 is the fission yield curve obtained, with the ^{235}U 14-MeV fission yield curve and the ^{238}U 16-MeV photofission curve superimposed for comparison.

TABLE 1.—OBSERVED VALUES OF FISSION YIELDS FOR ^{238}U 14-MeV NEUTRON FISSION

Mass no.	Nuclide measured	Fission yield (%)
89	Sr	2·30 ± 0·12
91	Y	2·78 ± 0·14
99	Mo	5·58 ± 0·28
111	Ag	0·81 ± 0·04
115	Cd (54 hr)	0·58 ± 0·03
115	Cd (43 day)*	0·06 ± 0·01
115	Cd (total chain)	0·64 ± 0·04
140	Ba	4·41 ± 0·22
143	Ce	3·91 ± 0·27
143	Pr	3·16 ± 0·16
144	Ce	2·68 ± 0·16
147	Nd	1·99 ± 0·10
153	Sm	0·39 ± 0·02
156	Eu	0·13 ± 0·01

* Estimated

A value of 4 for the number of prompt fission neutrons emitted has been used in order to plot the mirror points. This is the value which gives the best fit for them. Since no absolute values have been obtained, the curve has been drawn so that the area under it sums to 200 per cent, giving an absolute value for the fission yield of ^{99}Mo of 5·58 per cent. It should be noted, however, that no values are available for fission yields between mass 99 and 111 and hence the shape of this part of the curve may not be correct. This introduces an error of about ±10 per cent in the absolute value for ^{99}Mo. The peak-to-trough ratio is seen to be 9·1.

DISCUSSION

Shape of Curve

The fission yields plotted in Fig. 1 are compared with the curve for ^{235}U obtained from the published results of SPENCE[4] and WAHL[7] referred to ^{99}Mo = 5·17 per cent[5] and to the 16-MeV photofission curve for ^{238}U of RICHTER and CORYELL.[3]

Position of Peaks

From a comparison of the two 14-MeV fission curves, it can be seen that the light peak of the ^{238}U curve has shifted 3–4 mass units towards the heavy peak, which is substantially unmoved. This effect has been observed before[13] and is attributed to the stabilizing influence of the 82-neutron shell. The position of the heavy peak in the ^{238}U photofission curve is, at first sight, anomalous, but on examination it is seen that it is virtually in the same place, (around mass 135), but there is a falling away of the

[13] C. D. CORYELL and N. SUGARMAN *National Nuclear Energy Series* Vol. 9B. p. 543. McGraw-Hill, New York (1951).

heavy shoulder of this peak in both the 14-MeV curves compared with it. In addition to this, the photofission curve is distorted by fine structure at mass 133. If (with CORYELL) 3 prompt neutrons are assumed per fission, the light peak of the photofission

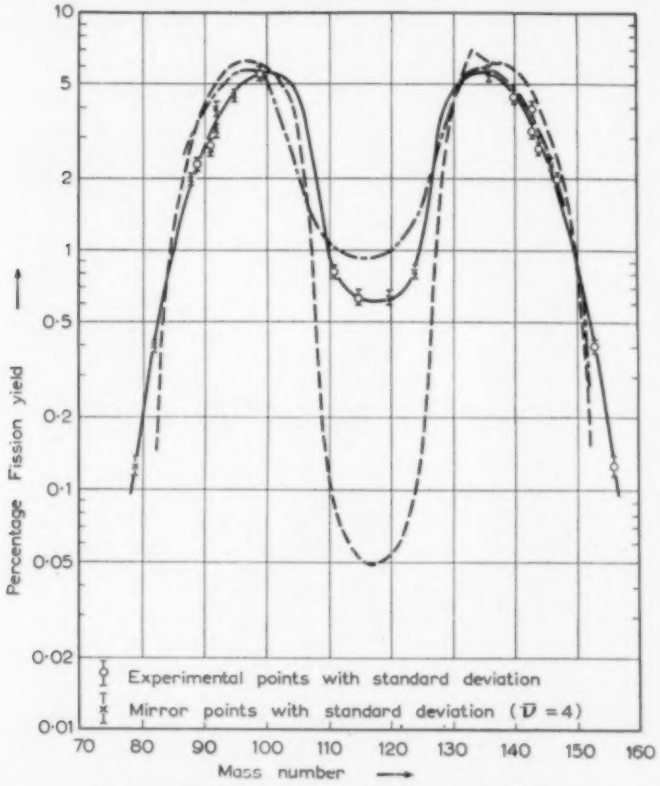

FIG. 1.—Fission yield curve, uranium-238 with 14-MeV neutrons.
——— ^{238}U 14 MeV.
— · — ^{235}U 14 MeV.
– – – – ^{238}U 16 MeV.
Photofission.

curve would be expected to be in the same position as the ^{238}U 14-MeV curve. In fact, this is not the case, and it is difficult to see why not, unless RICHTER and CORYELL's value for ^{99}Mo is low.

Average Number of Prompt Neutrons Emitted per Fission ($\bar{\nu}$)

A very rough estimate of the value of $\bar{\nu}$ can be made by plotting the mirror points, as has been done in Fig. 1. It is obvious that whereas the value of $\bar{\nu} = 4$ used to calculate the mirror points allows them to fit in well with the experimental points, a value of 3 or 5 would be a much poorer fit. Thus a rough value of $(4 \pm 0{\cdot}5)$ is obtained for $\bar{\nu}$.

Peak-to-trough Ratio

The peak-to-trough ratio for ^{238}U 14-MeV fission is seen to be 9·1, compared with about 6·6 for ^{235}U 14-MeV fission, although these values are extremely sensitive to the

value for the yield of the 115 chain. The ratio for ^{235}U thermal fission is approximately 600, the great decrease for 14-MeV being attributed to the lessening influence of the 82-neutron shell as more energy is put into the fissioning nucleus. The ratio for 16-MeV γ fission* of ^{238}U is, however, very much larger than that for 14-MeV neutrons, presumably because the binding energy of the extra neutron in 14-MeV fission has to be added to the available excitation energy.

Fine Structure

The ^{238}U 14-MeV curve has not sufficient points to show whether or not fine structure exists in 14-MeV fission, but RICHTER and CORYELL's photofission curve clearly shows fine structure at mass 133. WAHL's results[7] for ^{235}U 14-MeV fission show fine structure around mass 134 and it is to be expected that it is also present in ^{238}U. It is clearly desirable that fission yields of ^{131}I–^{135}I should be measured to examine this point.

CONCLUSIONS

The results presented for the 14-MeV neutron fission of natural uranium give the general shape of the ^{238}U fission yield curve and some information concerning prompt neutron emission and absolute yields, but more measurements are needed to establish the details, particularly as regards fine structure.

Acknowledgements—The author wishes to thank Dr. M. J. POOLE and Mr. I. JOHNSTONE of the Nuclear Physics Division at A.E.R.E. for conducting the irradiations and for many helpful discussions concerning them.

* It should be noted that although the maximum photon energy was 16 MeV, the effective photon energies were principally 9–14 MeV.

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HALF-LIFE OF ^{238}Pu*

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Abstract—The half-life of ^{238}Pu has been measured by determining its rate of growth from ^{242}Cm. The weighted average of two determinations is 86·41 years, with an estimated error of 0·3 year.

SEVERAL values for the half-life of ^{238}Pu have been reported in the literature. JAFFEY and MAGNUSSON[1] reported 77 years from the ratio of ^{238}Np β-activity to the measured growth of ^{238}Pu α-activity; JAFFEY[2] obtained a value of 89 ± 9 years by direct decay measurements, and JAFFEY and LERNER[3] later obtained $89{\cdot}59 \pm 0{\cdot}37$ years by a direct decay method. SEABORG, JAMES, and GHIORSO[4] determined the half-life by growth of the ^{238}Pu α-activity from its ^{242}Cm parent. Their value of 92 ± 2 years for the half-life was calculated using a ^{242}Cm half-life of 150 days.

Since there is a large spread in the reported values for the ^{238}Pu half-life, and a very accurate value for the ^{242}Cm half-life[5] is now available, it seemed worthwhile to repeat the determination of the ^{238}Pu half-life by measuring its growth from ^{242}Cm as accurately as possible.

EXPERIMENTAL PROCEDURE

Analyses of curium

The ^{242}Cm† used in the following experiments was produced by thermal neutron irradiation of ^{241}Am. An initial hot lactate cation resin column was used to separate the bulk of the americium from the curium.

The results of a mass spectrometric analysis performed by the Argonne National Laboratory on an aliquot of this curium from which the remaining americium had been removed by elution from a cation resin column with ammonium α-hydroxy-*iso*butyrate,[6] are presented in Table 1. The α-activity from ^{243}Cm and ^{244}Cm, corrected to 12 July 1955, the time of standardization of the curium solutions, was calculated to be 0·88 per cent of the ^{242}Cm α-activity.

α-pulse analyses of an electroplated sample of the curium gave an average value of 0·64 per cent for the ^{243}Cm and ^{244}Cm α-activity relative to the ^{242}Cm activity

* Work done under the auspices of the U.S. Atomic Energy Commission.

† The authors are indebted to Dr. R. A. PENNEMAN of this Laboratory for making available for the experiments a portion of the ^{243}Cm sample on which the calorimetric measurements of the ^{242}Cm half-life were performed.

[1] A. H. JAFFEY and L. B. MAGNUSSON *The Transuranium Elements* (Edited by G. T. SEABORG, J. J. KATZ, and W. M. MANNING). Paper No. 14.2. *National Nuclear Energy Series, Plutonium Project Record* Div. IV. Vol. 14B. Part II. p. 978. McGraw-Hill, New York (1951).

[2] A. H. JAFFEY *Ibid.* Paper No. 2.2. Part I. p. 89.

[3] A. H. JAFFEY and J. LERNER Reported in Argonne National Laboratory Classified Report ANL-4411 (1950).

[4] G. T. SEABORG, R. A. JAMES, and A. GHIORSO *The Transuranium Elements* (Edited by G. T. SEABORG, J. J. KATZ, and W. M. MANNING) Paper No. 22.2. *National Nuclear Energy Series, Plutonium Project Record* Div. IV. Vol. 14B. Part II. p. 1554. McGraw-Hill, New York (1951).

[5] R. A. PENNEMAN, L. H. TRIEMAN, and B. BEVAN Private communication.

[6] H. L. SMITH and D. C. HOFFMAN *J. inorg. nucl. Chem.* **3**, 243 (1956).

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TABLE 1.—CURIUM MASS ANALYSIS (7 March 1956)

Isotope	Atom (per cent)	$T_{\frac{1}{2}}$
^{243}Cm	36·3 ± 0·7	162·7 days[5]
^{242}Cm	57·0 ± 0·7	35 years[7]
^{244}Cm	6·7 ± 0·2	18·4 ± 0·5 years[8,9]
^{245}Cm	<0·08	

(Table 2). The average value of the pulse analyses and the mass spectrometric data is 0·76 per cent, with an estimated uncertainty of 0·1 per cent.

After decay of 54 per cent of the ^{242}Cm and removal of the ^{238}Pu produced, the average of several α-pulse analyses indicated 0·204 per cent ^{241}Am α-activity, or 0·09 per cent at the time of standardization. Therefore, in subsequent calculations,

TABLE 2.—CURIUM PULSE ANALYSES

Date of α-pulse analysis	$\frac{^{243,244}Cm\ \alpha\text{-activity}}{^{242}Cm\ \alpha\text{-activity}}$ (per cent)	
	On date of pulse analysis	Corrected to 12 July 1955
10 January 1956	1·31* ± 0·2	0·60 ± 0·1
26 March 1956	2·03* ± 0·3	0·68 ± 0·1
3 May 1956	2·30	0·65
	Average:	0·64

* Average of two analyses.

a total correction of 0·85 per cent with an estimated standard deviation, *s*, of 0·2 per cent, was subtracted for the contribution of ^{243}Cm, ^{244}Cm, and ^{241}Am to the α-counting rate of the ^{242}Cm standards.

Preparation of ^{242}Cm standard solutions

Experiment I. An aliquot of the curium stock solution was saturated with HCl gas and passed through three successive Dowex AGl-XlO anion-exchange resin columns to remove plutonium. The time of the last plutonium separation was 1015 on 12 July 1955. Solution Cm IA was prepared from the purified curium by dilution to about 25 ml with 3N HCl. From this, two "B" dilutions of eactly 3 ml to 100 ml were prepared, and from each, 1 ml standards were aliquoted on to $1\frac{7}{8}$ in. platinum discs(*) and α-counted on each of two different 2π methane-flow proportional

* Kimble Normax retested volumetric flasks and transfer pipettes complying with the specifications of NBS Circular C-434 were used in all cases. The limit of error for Normax 100 ml volumetric flasks is 0·08 per cent and was considered, therefore, to be negligible. The limit of error is 0·006 ml for 1 and 2 ml pipettes, and 0·01 ml for 3 ml pipettes. However, a new pipette was used for each pipetting, so that variation in content of pipettes is on the same basis as other errors and is, therefore, included in *s*. In the case of the standards which were pipetted directly onto platinum, the pipettes were drained to a level determined by first draining the pipette into a glass vessel in the standard manner.

[7] F. ASARO UCRL-2180, June, 1953 (Unpublished).
[8] C. M. STEVENS, M. H. STUDIER, P. R. FIELDS, J. F. MECH, P. A. SELLERS, A. M. FRIEDMAN, H. DIAMOND, and J. R. HUIZENGA *Phys. Rev.* **94**, 974 (1954).
[9] A. M. FRIEDMAN, A. L. HARKNESS, P. R. FIELDS, M. H. STUDIER, and J. R. HUIZENGA *Ibid.* **95**, 1501 (1954).

counters. The standards were prepared from "B" dilutions to avoid the necessity for making coincidence counting-loss corrections. The standards appeared to be essentially mass-free, so no absorption corrections were made. The average of three such samples from dilution IB-1, and two from dilution IB-2 was 9350·6 counts/min, with a standard deviation, s,* of 6·4 counts/min for this average. The overall spread was only 0·4 per cent. Results from the two different α-counters were averaged, since they seemed to give identical results. After making the 0·85 per cent correction for ^{241}Am, ^{243}Cm, and ^{244}Cm, the counting rate of ^{242}Cm in the Cm IA solution was calculated to be 309,037 counts per min per ml, or 309,334 counts per min per ml corrected to 1015 on 12 July 1955, the zero time of the experiment.

Experiment II. Another aliquot of the same curium stock solution was passed through an HCl action column to separate any lanthanum that might be present. Four anion resin columns were then used to remove the plutonium. "A" and "B" dilutions were prepared, standardized, and counted exactly as in Experiment I. The average of seven 1 ml samples from the "B" dilutions was 11,681·5 counts/min, with $s = 3·9$ counts/min and an over-all spread of 0·18 per cent. Therefore, the Cm IIA solution contained 386,445 counts/min/ml of ^{242}Cm corrected to the zero time of the experiment.

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^{238}Pu *analyses*

In order to determine whether any ^{238}Pu had been left in the curium after purification, four 2 ml aliquots from each of the standard solutions, Cm IA and IIA, were traced with 1 ml aliquots of a standardized ^{239}Pu tracer† solution of appropriate strength and were analysed by a standard plutonium procedure.‡ Briefly, the procedure consists of a LaF_3 precipitation followed by dissolution of the precipitate in H_3BO_3 and concentrated HCl, and adsorption of the plutonium on a Dowex AGl-X10 anion resin column which is washed with many column volumes of concentrated HCl to remove all traces of curium. The plutonium is then eluted from the column with a 0·25M HI solution saturated with HCl gas and electroplated on a 1 in. platinum disc. The samples were α-pulse analysed to determine the ratio of ^{238}Pu to the ^{239}Pu tracer. Since these electroplated samples were essentially mass-free and the ratio of ^{238}Pu to ^{239}Pu α-activity was $\leq$20 per cent (see Table 3), any correction for the contribution to the ^{239}Pu α-peak because of tailing from the higher-energy ^{238}Pu peak was small. By calculating the appropriate tail-to-peak ratio for the ^{239}Pu in the samples and assuming that the ratio would be the same for the ^{238}Pu, this correction was found to be $\leq$0·2 per cent of the ^{238}Pu-to-^{239}Pu ratio in all cases. At intervals during the course of these and subsequent analyses, two electroplated standards of known ^{238}Pu-to-^{239}Pu ratios (0·0990 and 0·1990 containing 14,737 and 7414

* s was calculated from the following formula: $s^2 = \sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n(n-1)}$ where x_i = counting rate of sample i, $\bar{x} = \sum_{i=1}^{n} \frac{x_i}{n}$, and n = number of samples. The counting standard deviations were much lower than the s calculated from the above formula, since it includes other errors such as in pipetting and dilution, and is really a measure of the consistency of the data.

† Three ^{239}Pu standard tracer solutions of various strengths were prepared from ^{239}Pu which had been shown by mass spectrometric and α-pulse analysis to be free of other plutonium α-emitters. The solutions were standardized (see footnote *, p. 7) and s was calculated in the same manner as for the ^{243}Cm standard solutions.

‡ J-11 collected Radiochemical Procedures (Radiochemistry Group J-11) LA-1721.

counts/min, respectively) were pulse analysed to check the performance of the equipment and our method of data analysis. These standards were electroplated from solutions prepared by mixing known aliquots of ^{238}Pu and ^{239}Pu solutions standardized by the techniques previously described for the ^{242}Cm and ^{239}Pu standard solutions. The ratios obtained from pulse analysis (counting standard deviations $\leq$0·3 per cent) of these standards agreed with the known ratios to 0·3 per cent or better.

TABLE 3.—^{238}Pu ANALYSES

	Time since initial Cm purification (hours)	Activity ratio* ($^{238}Pu/^{239}Pu$)	^{238}Pu (counts/min/ml)	s† (counts/min/ml)
Cm IA	0	0·1904	0·45	0·045
	2043·83	0·1228	485·19	1·42
	4055·67	0·1040	821·72	1·82
Cm IIA	0	0·1082	0·08	0·08
	2043·22	0·0690	603·73	0·975
	4055·88	0·1157	1018·32	2·82

* These ratios are the average of the pulse analyses for the four aliquots analysed at each of the times listed in the table.

† This standard deviation was calculated by combining s for the activity ratio (s was again calculated from the formula given in the footnote, page 6) with s for the ^{239}Pu tracer by the usual rule for the propagation of errors. The counting standard deviations of the pulse analyses account for most of the s for the 0 time analyses, since the counting rates were so low. In the other analyses, totals of ~130,000 to ~50,000 α-counts were collected over the ^{239}Pu peak for each aliquot, so the counting standard deviations for the average of the four aliquots were ~0·05 per cent to ~0·2 per cent, and account for only about half of s.

The separation time for Cm IA was 27·92 hours after the initial purification and, therefore, 7·88 counts/min/ml of ^{238}Pu should have grown from the ^{242}Cm. The separation time was 29·92 hours for Cm IIA, and 9·39 counts/min/ml of ^{238}Pu should have been found. An average of 8·33 counts/min/ml ($s = 0·045$) was found in IA, and 9·47 counts/min/ml ($s = 0·08$) in IIA. Apparently then, 0·45 counts/min/ml ($s = 0·045$) of ^{238}Pu remained in IA, and 0·08 counts/min/ml ($s = 0·08$) of ^{238}Pu remained in IIA after purification. These values were later subtracted (Table 4) from the ^{238}Pu activity found in the analyses at 85 and 168 days in order to simplify the numerical work involved in the calculation of the results. The standardized solutions were sealed to prevent evaporation until the next analyses.

In the subsequent analyses four 1 ml aliquots were taken from each of the standard solutions, Cm IA and IIA, at each time, and were traced with ^{239}Pu and analysed for ^{238}Pu as previously described. Table 3 summarizes these results.

The separation time from curium was taken as the time when the sample had just passed through the anion column, since the plutonium is adsorbed on the top and the curium runs through. It required only about 5 min to pass the sample solution through the column, so the uncertainty in separation time is small; s is taken to be 5 min.

TABLE 4.—QUANTITIES USED IN THE LEAST-SQUARES CALCULATIONS

Symbol	Meaning	*Experiment* I	II
X_1	$\varepsilon\lambda_1 N_1(0)$	309,334 counts/min/ml	386,445 counts/min/ml
X_2	$\varepsilon\lambda_2 N_2(0)$	0	0
X_3	$\varepsilon\lambda_2 N_2(X_4)$, First measured counting rate	484·74 counts/min/ml	603·65 counts/min/ml
X_4	Time of first growth measurement	2043·83 hours	2043·22 hours
X_5	$\varepsilon\lambda_2 N_2(X_6)$, Second measured counting rate	821·27 counts/min/ml	1018·24 counts/min/ml
X_6	Time of second growth measurement	4055·67 hours	4055·88 hours
W_1	Weight of: X_1	$2{\cdot}33 \times 10^{-6}$	$1{\cdot}65 \times 10^{-6}$
W_2	X_2	494	156
W_3	X_3	0·492	1·05
W_4	X_4	144	144
W_5	X_5	0·311	0·126
W_6	X_6	144	144
Final result for $T_{\frac{1}{2}}$ of ^{238}Pu		86·10 years	86·64 years
Standard deviation		0·24 years	0·21 years
Weighted average for $T_{\frac{1}{2}}$ of ^{238}Pu		86·41 years	
Standard deviation		0·16 years	

TREATMENT OF DATA

The data were treated by the least-squares method of DEMING.[10] The equation for ^{238}Pu activity is:

$$\varepsilon\lambda_2 N_2(t) = \frac{\varepsilon\lambda_1 N_1(0)\lambda_2}{\lambda_2 - \lambda_1}(e^{-\lambda_1 t} - e^{-\lambda_2 t}) + \varepsilon\lambda_2 N_2(0)e^{-\lambda_2 t}$$

where the symbols have their usual meaning. The subscript 1 refers to ^{242}Cm and subscript 2 refers to ^{238}Pu. ε is the counting efficiency of ^{238}Pu and is assumed to be the same as for ^{242}Cm. Some of the symbols used in the DEMING treatment (ref. 10, Chap. IV) are identified in Table 4. The parameter evaluated is a for λ_2. The half-life of ^{242}Cm was assumed, for the calculation, to be exactly 162·7 days.* The equations of condition are:

$$F^1 = X_3 - \frac{X_1 a}{a - \lambda_1}(e^{-\lambda_1 X_4} - e^{-aX_4}) - X_2 e^{-aX_4}$$

$$F = X_5 - \frac{X_1 a}{a - \lambda_1}(e^{-\lambda_1 X_6} - e^{-aX_6}) - X_2 e^{-aX_6}$$

The half-lives from the two experiments and their standard deviations from the least-squares calculation are given in Table 4. We do not know the probability density function of the minimized sum of squares of the deviations and are, therefore, unable to apply tests such as the χ^2 test or to estimate σ^2 by external consistency.

* The estimated error of this half-life is 0·1 day.[5] An approximate calculation indicates that using a number 0·1 day different would change the ^{238}Pu half-life by less than 0·01 year.

[10] W. E. DEMING *Statistical Adjustment of Data* (First Edition) John Wiley, New York (1948).

RESULTS

The half-lives from the two experiments do not agree to within their standard deviations (Table 4). Experiment 1 gave 86·10 years, with a standard deviation, s, of 0·24 years, while Experiment 2 gave 86·64 years, $s = 0·21$ years. The standard deviations of the half-lives may be too small because of underestimation of the standard deviations of the data going into the calculation. However, the weighted average of 86·41 years, $s = 0·16$ years, is estimated to be correct to within about 0·3 years, but is in relatively poor agreement with the value of $89 \pm 0·37$ years reported by JAFFEY and LERNER.[3]

Our data do not appear to indicate any systematic bias. However, a difference in the α-counting efficiency of the proportional counters for ^{238}Pu and ^{242}Cm, or an error in the determination of the isotopic purity of the ^{242}Cm used in the experiments would influence the answers, but would not be apparent as trends in the data. The error of 0·3 years was estimated to include these possible systematic errors.

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THE OCCURRENCE OF THE SHORT-LIVED IODINE ISOTOPES IN NATURAL AND IN DEPLETED URANIUM SALTS*†

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Abstract—The occurrence of the short-lived iodine isotopes in non-irradiated uranium salts has been established. The equilibrium ratios of the short-lived iodine isotopes to ^{238}U in depleted uranium agree, within the experimental error, with the ratios in natural uranium. The ratios expressed in terms of 10^{-4} disintegrations per second per gram of ^{238}U are: ^{131}I, $0{\cdot}3 \pm 0{\cdot}1$; ^{132}I, $2{\cdot}5 \pm 0{\cdot}3$; ^{133}I, $1{\cdot}0 \pm 0{\cdot}2$; ^{134}I, $3{\cdot}6 \pm 0{\cdot}4$; ^{135}I, $3{\cdot}5 \pm 0{\cdot}4$. The following values are obtained for the yields of the iodine isotopes, if SEGRÈ's value for the spontaneous fission half-life of ^{238}U, $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years, is taken to be correct: ^{131}I, $0{\cdot}4 \pm 0{\cdot}1$; ^{132}I, $3{\cdot}6 \pm 0{\cdot}4$; ^{133}I, $1{\cdot}5 \pm 0{\cdot}3$; ^{134}I, $5{\cdot}2 \pm 0{\cdot}5$; ^{135}I, $5{\cdot}1 \pm 0{\cdot}5$ per cent.

THE isotopic composition of the rare gases krypton and xenon produced in various minerals by spontaneous and induced fission of uranium has been studied by FLEMING and THODE[1] and by WETHERILL[2] in 1953, using the highly sensitive mass-spectrometric technique.

The radiochemical method, which supplies more detailed information on the distribution of mass and charge in fission, has been applied to the study of spontaneous fission of ^{242}Cm by STEINBERG and GLENDENIN[3] in 1954. However, the radiochemical method has never been successfully applied to the study of spontaneous fission of ^{238}U, since the extremely slow rate of decay by this process in uranium does not provide sufficient fission activity for accurate measurements. It has been pointed out by these investigators that at least a ton of ^{238}U would be required to obtain a measurable activity of a fission product with a yield of 0·01 per cent, whereas only 1 mg of ^{242}Cm would suffice.

In spite of the obvious difficulties involved in the radiochemical investigation of the spontaneous fission of ^{238}U, however, it was felt worthwhile to investigate the problem in greater detail for the following reasons: (a) the mass-yield curve for the spontaneous fission of ^{242}Cm should be different from that of ^{238}U, (b) the radiochemical method should supply more detailed and direct information on the mass distribution in spontaneous fission of ^{238}U, as well as the spontaneous fission rate of ^{238}U, than the mass spectrometric method, and (c) the experimental techniques used in the study of the spontaneous fission of ^{238}U may later prove to be useful in the study of geochemical problems, such as the determination of the ratio of the induced fission to the spontaneous fission in natural uranium ores.

* This paper represents a part of the dissertation to be submitted by F. T. ASHIZAWA to the Graduate School of the University of Arkansas in partial fulfilment of the requirement for the degree of Master of Science.

† Presented at the Southwide Chemical Conference, 6 December 1956, Memphis, Tennessee.

[1] W. H. FLEMING and H. G. THODE *Phys. Rev.* **92**, 378 (1953).

[2] G. W. WETHERILL *Phys. Rev.* **92**, 907 (1953).

[3] E. P. STEINBERG and L. E. GLENDENIN *Phys. Rev.* **95**, 431 (1954).

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This paper deals with the occurrence of the short-lived iodine isotopes in non-irradiated natural and depleted uranium salts.

It has to be pointed out that the problem was first studied by LIBBY,[4] as early as 1939, prior to the discovery of the phenomenon of spontaneous fission. However, LIBBY was unable to identify the iodine activity in non-irradiated uranium salts and he reported a lower limit for the natural fission half-life of uranium.

The first successful isolation and identification of the short-lived iodine isotopes from non-irradiated natural uranium salt was reported by the authors and R. R. EDWARDS[5] in 1956. It has been shown in the preliminary report that a value of $(1{\cdot}03 \pm 0{\cdot}10) \times 10^{16}$ years is obtained for the spontaneous fission half-life of ^{238}U, under the following assumptions: (a) the average fission yield for ^{131}I, ^{133}I and ^{135}I is 3 per cent, (b) the contribution of the induced fission is negligibly small, and (c) the interchange between the fission iodine and the added iodine carrier is complete.

At least one of the major uncertainties mentioned above has been eliminated in the present study, in which the measurements were made with natural and with depleted uranium.

Another improvement made in the present study was the use of an extremely stable low-level counting equipment. The background of the counter used was practically constant at $1{\cdot}05 \pm 0{\cdot}05$ c/min throughout the year.

One of the major problems which was not fully investigated was the phenomenon of the incomplete interchange between the fission iodine and the added iodine carrier. STEINBERG and GLENDENIN[3] have reported that the fission iodine recoveries from the ^{242}Cm solution were only approximately 67 per cent of the expected value. They pointed out the possible effect of H_2O_2 formed in the solution by the intense radiation from ^{242}Cm. No such problem should exist in the experiments with natural and with depleted uranium. However, a large quantity of uranium which had to be treated in the present study made it impossible to use the NaClO method, recommended by GLENDENIN and METCALF.[6] Instead, the periodate carrier method, which has been shown to give neither complete nor reproducible interchange between the fission iodine and the added carrier was used in this study.

According to GLENDENIN and METCALF, the procedure involving the addition of carrier as IO_4^- and the reduction to I^- with $NaHSO_3$ in dilute acid solution gives separation of the 2·4 hr iodine from the stock solution varying from 65 to 95 per cent in efficiency. Although several investigators have made similar observations, the phenomenon does not seem to be thoroughly understood.[7,8]

A 100 per cent interchange between the spontaneous fission iodine and the added periodate carrier is assumed in this paper and the spontaneous fission yields of the iodine isotopes thus obtained are compared with the stable xenon isotope yields reported by WETHERILL.[2]

EXPERIMENTAL

Natural uranium solution. A total of 1400 ± 10 g of uranium extracted from Belgian Congo pitchblende and exhaustively purified, was dissolved in 10 l. of 1 N nitric acid.

Depleted uranium solution. A total of 1600 ± 10 g of depleted uranium was dissolved in 8 l. of 1 N nitric acid. The isotopic composition of the depleted uranium was 0·011 per cent ^{235}U and 99·989

[4] W. F. LIBBY *Phys. Rev.* **55**, 1269 (1939).
[5] P. K. KURODA, R. R. EDWARDS, and F. T. ASHIZAWA *J. chem. Phys.* **25**, 603 (1956).
[6] L. E. GLENDENIN and R. P. METCALF *Radiochemical Studies: The Fission Products* Paper 140 (1951).
[7] W. H. BURGUS and T. H. DAVIES *Radiochemical Studies: The Fission Products* Paper 19 (1951).
[8] T. C. HOERING Private communication.

per cent ^{238}U, according to Dr. R. B. MARTIN of the U. S. Atomic Energy Commission, Oak Ridge, Tennessee.

Counting equipment. A pancake type Geiger-Müller counter (Anton 1007TA, 2 mg/cm^{-2} mica window), which had a background of 1·05 ± 0·05 counts/min in anticoincidence with the surrounding counters, was used for the radioactivity measurements. An end-window Geiger-Müller counter (RCL 1–3 H, 3·3 mg/cm^{-2} mica window) was also used in the preliminary experiments.

The counters were calibrated using a standard sample of chlorine-36 prepared and calibrated by Professor BEROL L. ROBINSON of the Department of Physics, by the 4π counting method. The effect of the self-absorption was checked by counting various beta-active isotopes in various amounts of carriers.

Extraction and purification of the short-lived iodine isotopes. The iodine carrier (30 mg I as KIO_3 and KIO_4*) was added to the acidic solution of uranium. The periodate and iodate ions were then reduced by the addition of sodium sulphite solution, and then oxidized to I_2 with sodium nitrite. The iodine carrier was extracted twice with 400 ml portions of carbon tetrachloride and discarded. The uranium solution was then allowed to stand for certain intervals of time (30 min, 6 hr, 21 hr, 6 days, 15 days, or 30 days).

The iodine carrier (30 mg I as KIO_3 and KIO_4) was again added to the uranium solution, reduced by the addition of sodium sulphite, and oxidized to I_2 with sodium nitrite. The iodine carrier was extracted with carbon tetrachloride (twice with 400 ml portions), and the carbon tetrachloride layer was transferred into a separatory funnel, washed with 50 ml of 0·5 N nitric acid and finally with 100 ml of water. The carbon tetrachloride layer was transferred into another separatory funnel, which contained 50 ml of 0·1 M ammonium sulphite solution adjusted to pH = 10. The iodine isotopes were extracted into the aqueous sulphite layer and the carbon tetrachloride layer was discarded.

A 20 ml portion of a mixed chloroform solution of dithizone (0·025 per cent) and 8-hydroxyquinoline (0·5 per cent) was added to the aqueous layer, and the solution was shaken in a separatory funnel. The chloroform layer was discarded, and the aqueous layer was washed four times with 20 ml portions of chloroform. The aqueous solution was filtered through a small filter paper and the filtrate was collected into a small beaker.

The iodine was finally precipitated by the addition of 2 ml of 6 N nitric acid and a slight excess of the 0·1 N silver nitrate solution. The silver iodide precipitate was filtered onto a small filter paper disk, and washed with water and acetone. The dried precipitate was weighed, mounted on aluminium planchette, and counted.

Control experiments. Assuming the contribution of the neutron-induced fission is negligible, the amounts of the short-lived iodine isotopes expected to be present in non-irradiated uranium salts can be calculated from the following equation:

$$\text{Iodine activity/uranium activity} = T_{1/2\alpha}/T_{1/2f} \cdot y \qquad (1)$$

where $T_{1/2\alpha}$ is the alpha-decay half-life, $T_{1/2f}$ is the spontaneous fission half-life of ^{238}U, and y is the spontaneous fission yield of the iodine isotope in question.

A simple calculation yields a value of 1×10^{-14} curie ^{134}I per gram of ^{238}U, assuming a value of $y = 5$ per cent for ^{134}I. This corresponds to 1·7 atoms of ^{134}I per gram of ^{238}U, or 2400 atoms per 1400 g of ^{238}U.

The natural uranium solution containing 1400 g of ^{238}U was allowed to stand for 30 min after the initial removal of the iodine carrier. According to WAHL,[9] the independent thermal neutron-induced fission yield of ^{134}I is 0·89 per cent or 11 per cent of the total chain yield. The independent ^{238}U spontaneous fission yield of ^{134}I is unknown, but it is probably small and ^{134}I is most likely formed by the ^{134}Te decay, rather than directly by the ^{238}U fission. Since the tellurium isotopes were not removed from the uranium solution, the equilibrium amount of ^{134}Te would have been always present in the solution. Thus, at least about 33 per cent of the equilibrium amount of ^{134}I would have been produced from ^{134}Te during the 30 min period, even though the amount of ^{134}I produced directly from ^{238}U may have been negligibly small.

The iodine carrier was added to the uranium solution after this period and the iodine was extracted with carbon tetrachloride, quickly purified, and counted. Approximately 790 atoms of ^{134}I would

* No significant difference was noted when KIO_4 alone was used, instead of a mixture of KIO_3 and KIO_4.

[9] A. C. WAHL *Phys. Rev.* **99**, 730 (1955).

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have been present in the iodine carrier at the time of extraction. Thus, the activity of the ^{134}I in the carrier at the time of separation must be $790 \times 0{\cdot}693/52 = 10{\cdot}5$ disintegrations per min. If one assumes the chemical yield to be 50 per cent and the over-all counting efficiency 10 per cent, the initial activity of the iodine carrier should be approximately 0·5 counts/min.

Aside from the ^{134}I, a small fraction of the equilibrium amount of ^{132}I would have been present in the iodine carrier. The initial activity of the ^{132}I was calculated to be approximately 0·14 counts/min, assuming a yield of $y = 3$ per cent, the same chemical yield and the same over-all counting efficiency.

The activities due to ^{131}I, ^{133}I and ^{135}I should be negligibly small, because the uranium solution was allowed to stand for only 30 min.

TABLE 1.—RADIOACTIVITY OF THE IODINE CARRIER EXTRACTED FROM A NATURAL URANIUM SOLUTION CONTAINING 1400 g OF ^{238}U AND 10 g OF ^{235}U. THE PANCAKE-TYPE COUNTER (BACKGROUND $1{\cdot}05 \pm 0{\cdot}03$ counts/min) WAS USED. CHEMICAL YIELDS: APPROXIMATELY 50 PER CENT

Time after the extraction	Observed activity counts/min	Iodine activity* counts/min
0	—	$0{\cdot}7 \pm 0{\cdot}1$†
0·5	$0{\cdot}57 \pm 0{\cdot}36$	0·51
0·75	$0{\cdot}45 \pm 0{\cdot}26$	0·39
2·8	$0{\cdot}28 \pm 0{\cdot}09$	0·22
15	$0{\cdot}18 \pm 0{\cdot}05$	0·12
29	$0{\cdot}05 \pm 0{\cdot}03$	—
38	$0{\cdot}09 \pm 0{\cdot}03$	—
72	$0{\cdot}06 \pm 0{\cdot}03$	—
97	$0{\cdot}03 \pm 0{\cdot}03$	—
130	$0{\cdot}07 \pm 0{\cdot}03$	—

* Observed activity less contamination (0·06 counts/min).
† Graphically obtained.

Thus, the initial activity of the iodine carrier should be $0{\cdot}50 + 0{\cdot}14 = 0{\cdot}64$ counts/min at the time of the iodine separation, and if the first radioactivity measurement was made 30 min after the iodine extraction, the observed activity at $t = 30$ min should be approximately 0·5 counts/min.

The counting results are shown in Table 1. The observed activity agreed with the calculated iodine activity. The slight residual activity ($0{\cdot}06 \pm 0{\cdot}03$) counts/min observed as a tail of the decay curve may have been the last trace of contamination, which was not completely removed by the decontamination procedure used.

In order to determine whether the activity which followed the iodine chemistry was really due to the fission iodine, the following additional control experiment was performed.

The iodine isotopes were extracted from the uranium solution and were purified according to the chemical procedure described earlier. The carriers of bismuth, aluminium, iron, barium, and strontium (10 mg each) were added to the sulphite solution of the iodine carrier, the acidity of the solution was adjusted to pH 1, and hydrogen sulphide gas was passed through the solution. The bismuth sulphide precipitate was filtered, washed, and dried. The filtrate was neutralized with ammonia, and the precipitate of iron and aluminium was filtered. The filtrate was then acidified, and the barium and strontium were precipitated as sulphates. The iodine carrier was finally precipitated as silver iodide. Practically all the activity was found in the iodine fraction, as shown in Table 2.

Reproducibility of the results. Although the periodate carrier method, which has been shown to give neither complete nor reproducible interchange between the fission iodine and the added carrier, was used in the present study, it was found that at least the experimental results obtained were unexpectedly reproducible. Table 3 shows the duplicate results obtained with the IO_4^- carrier.

Table 2.—Distribution of the activity among the added carriers

Carrier	Time after the iodine separation (hours)	Activity counts/min
Bi	1·0	0·08 ± 0·17
Fe and Al	1·5	0·00 ± 0·23
Ba and Sr	2·0	0·12 ± 0·17
I	5·0	2·3 ± 0·1
	12·0	1·4 ± 0·1

Table 3.—Reproducibility of the IO_4^- carrier method. The natural uranium solution, containing 1400 ± 10 g of ^{238}U and 10 g of ^{235}U, was allowed to stand for 6 hr. The end-window counter (background 15·0 ± 0·5 counts/min) was used for the radioactivity measurements

Time after the iodine extraction (hours)	Observed activity less background (counts/min)	
	Experiment IIa*	Experiment IIb†
0·8	9·8 ± 1·1	9·2 ± 1·1
1·6	6·7 ± 0·6	6·7 ± 0·6
3·4	3·9 ± 0·4	4·2 ± 0·4
5·0	2·8 ± 0·4	2·9 ± 0·4
12	1·8 ± 0·2	1·8 ± 0·2
19	1·0 ± 0·2	1·0 ± 0·2

* Chemical yield: 91 ± 1 per cent.
† Chemical yield: 91 ± 1 per cent.

Reasonably reproducible results were also obtained with the I^- carrier. However, the fission iodine recovery was found to be about 60 per cent of that obtained by the IO_4^- carrier method. The result seems to support the observation made by Burgus and Davies[7] that 60 to 75 per cent of the 2·4 hr I grown from 77 hr ^{132}Te is in the reduced chemical state.

Table 4.—Reproducibility of the I^- carrier method. The natural uranium solution, containing 1400 ± 10 g of ^{238}U and 10 g of ^{235}U, was allowed to stand for 6 hr. The end-window counter (background 15·0 ± 0·5 counts/min) was used

Time after the iodine extraction (hours)	Observed activity less background (counts/min)		
	Experiment IIc*	Experiment IId†	Experiment IIe‡
0·8	4·5 ± 0·7	4·5 ± 0·7	4·1 ± 0·7
1·6	2·9 ± 0·5	3·1 ± 0·5	2·6 ± 0·5
5·0	1·5 ± 0·3	1·5 ± 0·3	1·8 ± 0·3
10	0·8 ± 0·3	0·7 ± 0·3	1·2 ± 0·3
23	0·8 ± 0·3	0·7 ± 0·3	0·4 ± 0·3

* Chemical yield: 75 ± 1 per cent.
† 81 ± 1 per cent.
‡ 80 ± 1 per cent.

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RESULTS AND DISCUSSION

Iodine isotopes in natural uranium. The iodine isotopes were extracted from the natural uranium solution, which had been allowed to stand for 15 days after the previous iodine extraction, and were purified as described in the chemical procedure.

TABLE 5.—DECAY OF IODINE ISOTOPES FROM NATURAL URANIUM

Time after initial iodine separation		Observed activity (counts/min)	Observed activity less B.G. (counts/min)	Iodine activity* (counts/min)
Hours	1·5	5·95	4·90	4·84
	2·5	5·07	4·02	3·96
	3·5	4·88	3·83	3·77
	4·5	4·75	3·70	3·64
	5·5	3·88	2·83	2·77
	6·5	4·05	3·00	2·94
	7·5	3·63	2·57	2·51
	8·5	3·63	2·57	2·51
	11·0	3·18	2·13	2·07
	18·5	2·53	1·48	1·42
Days	1·1	2·02	0·97	0·91
	1·2	1·90	0·85	0·79
	1·7	1·62	0·57	0·51
	2·2	1·38	0·33	0·27
	2·7	1·32	0·27	0·21
	3·1	1·28	0·23	0·17
	3·8	1·24	0·19	0·13
	4·5	1·25	0·20	0·14
	5·9	1·21	0·16	0·10
	6·7	1·23	0·18	0·12
	7·7	1·25	0·20	0·14
	9·2	1·19	0·14	0·08
	11·7	1·18	0·13	0·07
	12·8	1·17	0·12	0·06
	13·7	1·15	0·10	0·04
	15·8	1·19	0·14	0·08
	17·2	1·15	0·10	0·04
	18·8	1·11	0·06	0·00
	19·8	1·14	0·09	0·03
	20·8	1·13	0·08	0·02
	22·2	1·13	0·08	0·02
	23·7	1·12	0·07	0·01
	25·2	1·15	0·10	0·03
	27·1	1·13	0·08	0·02
	30·0	1·13	0·08	0·02

* Observed activity, less B.G., less the 0·06 counts/min correction for the contamination.

The chemical yield was 95 per cent. The counting results are presented in Table 5 and in Fig. 1.

Iodine isotopes in depleted uranium. The iodine isotopes were extracted from the depleted uranium solution, which had been allowed to stand for 6 days after the

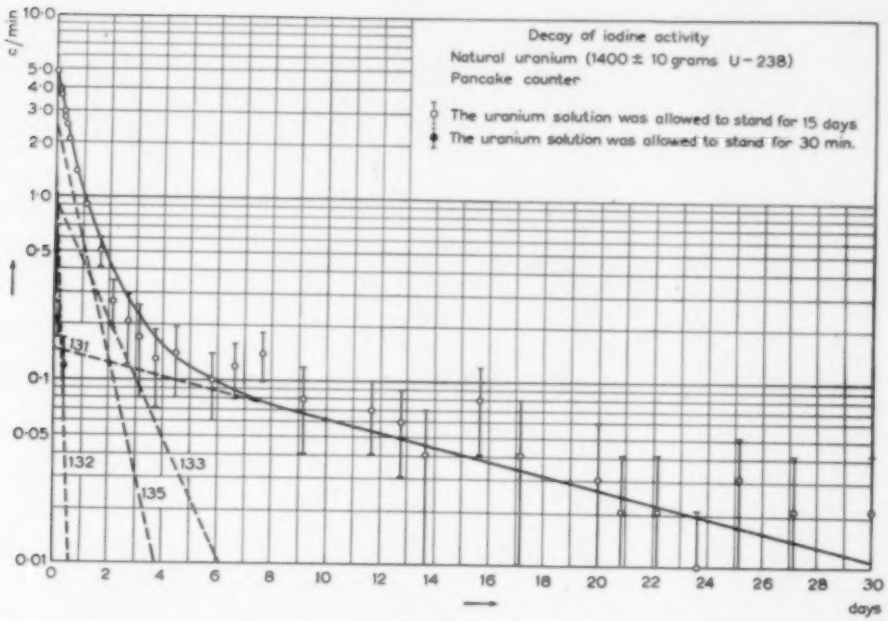

Fig. 1.

TABLE 6.—DECAY OF IODINE ISOTOPES FROM DEPLETED URANIUM

Time after initial iodine separation		Observed activity (counts/min)	Observed activity less B.G. (counts/min)	Iodine activity (counts/min)
Hours	1·0	7·67	6·61	6·55
	1·3	6·60	5·54	5·48
	2·0	5·45	4·39	4·33
	3·0	5·37	4·31	4·25
	4·0	5·15	4·09	4·03
	5·5	4·24	3·18	3·12
	8·0	3·87	2·81	2·75
	15·5	2·98	1·92	1·86
Days	1·1	2·38	1·32	1·26
	1·7	1·74	0·68	0·62
	2·5	1·43	0·37	0·31
	3·5	1·33	0·27	0·21
	4·5	1·23	0·17	0·11
	5·5	1·20	0·14	0·08
	8·5	1·15	0·09	0·03

* Observed activity, less B.G., less the 0·06 counts/min correction for the contamination.

previous iodine extraction, and were purified as described in the chemical procedure. The chemical yield was 97 per cent. The counting results are presented in Table 6.

The counting data shown in Table 5 and Table 6 are plotted together in Fig. 2. The results are corrected for the difference in the chemical yields and the amounts of ^{238}U used, and are expressed in terms of cpm of the total iodine activity per 1000 g of ^{238}U.

No difference was observed, within the counting errors, in the total activities, as well as in the shape of the decay curves, of the iodine isotopes extracted from natural

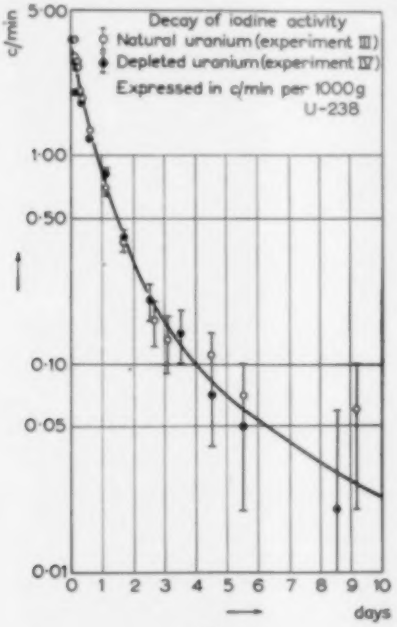

Fig. 2.

TABLE 7.—THE IODINE ISOTOPES/^{238}U EQUILIBRIUM RATIOS IN NATURAL AND IN DEPLETED URANIUM SOLUTION

Iodine isotopes	^{131}I	^{132}I	^{133}I	^{134}I	^{135}I
10^{-4} disintegrations per second per gram ^{238}U	$0{\cdot}3 \pm 0{\cdot}1$	$2{\cdot}5 \pm 0{\cdot}3$	$1{\cdot}0 \pm 0{\cdot}2$	$3{\cdot}6 \pm 0{\cdot}4$	$3{\cdot}5 \pm 0{\cdot}4$

and from depleted uranium. The results seem to indicate that the contribution of the induced fission of ^{235}U in natural uranium is small under the experimental conditions described above. Similar results were also obtained by PARKER and KURODA,[10] in the study of ^{99}Mo in natural and in depleted uranium salts.

Spontaneous fission yields of the iodine isotopes. The equilibrium activities of the individual iodine isotopes in the uranium solutions were calculated from the counting results of several experiments, in which the uranium solutions were allowed to stand for various intervals of time (6 hr, 21hr, 6 days, 15 days, or 30 days), and the results are shown in Table 7.

[10] P. L. PARKER and P. K. KURODA Presented at the Southwide Chemical Conference at Memphis, Tennessee. 6 December 1956.

The spontaneous fission yields of the iodine isotopes were then calculated from equation (1), taking SEGRÈ's value for the spontaneous fission half-life of ^{238}U, $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years,[11] to be correct. The results are shown in Table 8.

The yields of ^{131}I, ^{132}I and ^{134}I thus obtained agree unexpectedly well with the corresponding yields of ^{131}Xe, ^{132}Xe and ^{134}Xe reported by WETHERILL. Because of the assumed 100 per cent interchange between the fission iodine and the added iodine carrier, however, the agreement between the iodine yields and the xenon yields may

TABLE 8.—SPONTANEOUS FISSION YIELDS OF THE IODINE AND XENON ISOTOPES

Mass	131	132	133	134	135
Iodine yield	$0{\cdot}4 \pm 0{\cdot}1$	$3{\cdot}6 \pm 0{\cdot}4$	$1{\cdot}5 \pm 0{\cdot}3$	$5{\cdot}2 \pm 0{\cdot}5$	$5{\cdot}1 \pm 0{\cdot}5$
Xenon yield*	0·455	3·57	—	4·99	—

* Reported by WETHERILL.[2]

be fortuitous. In this connection, it is interesting to note that WETHERILL expressed his data relative to an assumed yield of 6·00 per cent for ^{136}Xe, while FLEMING and THODE[1] assigned an assumed value of 6·50 per cent to the ^{136}Xe yield.

The low value obtained for the ^{133}I yield is noteworthy. This gives a marked peak at the mass number 132 in the mass-yield curve, which might be related to the shell structure of the nuclide $^{132}_{50}Sn_{82}$, which is doubly magic.

The most probable charge Z_p for a given mass may be calculated according to the equal charge displacement rule of GLENDENIN, CORYELL, and EDWARDS:[12]

$$Z_p = Z_A - 1/2(Z_A + Z_{A^*} - Z_F) \tag{2}$$

where Z_A is the most stable charge for mass A, Z_F is the charge of the fissioning nucleus, and Z_{A^*} is the most stable charge for the complementary mass A^*; and

$$A^* = A_F - A - \nu \tag{3}$$

where A_F is the mass number of the fissioning nucleus, and ν is the average number of neutrons produced per fission ($\nu = 2{\cdot}2$ for ^{238}U spontaneous fission).

Using a value of 54·6 for Z_A at mass 132, equation (2) gives 45·5 for Z_{A^*}, corresponding to 103·8 for A^*, and a value of 50·6 for Z_p, which is not far apart from the Z value of ^{132}Sn.

It is interesting to note that if one takes the PERFILOV's value[13] for the spontaneous fission half-life of ^{238}U, $(1{\cdot}3 \pm 0{\cdot}2) \times 10^{16}$ years, to be correct, the following values have to be assigned to the iodine yields: ^{131}I, 0·6; ^{132}I, 5·8; ^{133}I, 2·4; ^{134}I, 8.4; ^{135}I, 8·1 per cent.

The multiplication constant of the uranium solution. The fact that no significant difference was observed between the fission iodine/^{238}U ratios in natural uranium and in depleted uranium deserves further consideration.

[11] E. SEGRÈ *Phys. Rev.* **86**, 21 (1952).
[12] L. E. GLENDENIN, C. D. CORYELL, and R. R. EDWARDS *Radiochemical Studies: The Fission Products* Paper 52 (1951).
[13] N. A. PERFILOV *J. exp. theor. Phys.* **17**, 476 (1947); *Chem. Abstr.* **42**, 2864 (1948).

It has been shown by FLEMING and THODE[1] and by WETHERILL[2] that considerable fractions of the xenon isotopes in pitchblende are formed by induced fission of uranium. This would mean that the multiplication constant of the natural assemblages of pitchblende is small, but measurable. The infinite multiplication constant of 20 samples of uraninite and pitchblende from various localities of the world has recently been calculated by KURODA.[14,15]

The infinite and effective multiplication constant of the uranium solutions used in the present study can be calculated in the following manner:

The infinite multiplication constant is,[16]

$$k_\infty = \varepsilon p f \eta = \varepsilon \,.\, \exp\left[-\frac{N_0}{\xi \Sigma_s} \int_E^{E_0} (\sigma_a)_{\text{eff}}\, dE/E \right] .$$

$$\cdot \frac{N_u(\sigma_a)_u}{N_u(\sigma_a)_u + N_m(\sigma_a)_m + N_1(\sigma_a)_1 + N_2(\sigma_a)_2 + \ldots\ldots} \cdot \frac{^{235}N(\sigma_f)_{235}}{^{235}N(\sigma_a)_{235} + {}^{238}N(\sigma_a)_{238}} \cdot \gamma \quad (4)$$

where ε is the fast fission factor, p is the resonance escape probability, f is the thermal utilization factor, η is the average number of fission neutrons produced per neutron absorbed by uranium, N_0 is the number of atoms of ^{238}U per cm^3, ξ is the average loss in logarithm of the neutron energy from an elastic collision, Σ_s is the macroscopic scattering cross-section of the moderator, $\int_E^E (\sigma_a)_{\text{eff}}\, dE/E$ is the effective resonance integral, N_u is the number of atoms of uranium per cm^3, N_m is the number of atoms of moderator (water) per cm^3, N_1, N_2 ... are the number of atoms of impurities per cm^3, (σ_a) is the microscopic thermal neutron absorption cross-section for material in question, ^{235}N is the number of atoms of ^{235}U per cm^3, ^{238}N is the number of atoms of ^{238}U per cm^3, $(\sigma_f)_{235}$ is the microscopic fission cross-section of ^{235}U, $(\sigma_a)_{235}$ is the microscopic absorption cross-section of ^{235}U, $(\sigma_a)_{238}$ is the microscopic absorption cross-section of ^{238}U, and γ is the average number of fast neutrons emitted per thermal fission of ^{235}U.

Neglecting the effect of added reagents and the impurities, one obtains from equation (4), a value of $k_\infty = 0{\cdot}13$ for an aqueous solution of natural uranium (1400 g uranium in 10 l. of 1 N nitric acid), and a value of $k_\infty = 0{\cdot}003$ for an aqueous solution of depleted uranium (1600 g ^{238}U in 8 l. of 1 N nitric acid).

The effective multiplication constant is

$$k_{\text{eff}} = k_\infty \,.\, L_f \,.\, L_t = k_\infty \,.\, e^{-K^2\tau} \cdot \frac{1}{(1 + K^2L^2)} \quad (5)$$

where, L_f is the fraction of fast neutrons which do not escape before becoming thermal, L_t is the fraction of thermal neutrons which do not get out before absorption, K^2 is the size-shape factor or "buckling", τ is the age or square of the fast diffusion length, and L is the thermal diffusion length. Simple calculations yield the following values for an aqueous solution of uranium placed in an approximately cylindrical container of radius $R = 15$ cm and height $H = 14$ cm: $L_f = 0{\cdot}084$ and $L_t = 0{\cdot}62$.

Hence, a value of $k_{\text{eff}} = 7 \times 10^{-3}$ is obtained for the natural uranium solution and a value of $k_{\text{eff}} = 1{\cdot}6 \times 10^{-4}$ for the depleted uranium solution.

[14] P. K. KURODA *J. chem. Phys.* **25**, 781 (1956).
[15] P. K. KURODA *J. chem. Phys.* **25**, 1295 (1956).
[16] R. STEPHENSON *Introduction to Nuclear Engineering* New York (1954).

Thus, it appears to be quite reasonable that no significant difference was observed between the fission iodine/^{238}U ratios in natural uranium and in depleted uranium.

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DIFFERENCE IN THE BEHAVIOUR OF THE ^{81}Se ISOMERS FOLLOWING NEUTRON CAPTURE

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Abstract—Experiments on neutron-irradiated selenium oxide in the solid state as well as in aqueous solution indicate a different chemical behaviour of the two selenium isomers, as a function of the physical state and of the neutron energy. The difference is shown in the activity ratios of the two isomers in the filtrate and the residue when passed through a sintered porcelain disc. These activity ratios are more significant than the absolute values of the retentions. If impurities have any effect it can only be to strengthen the hypothesis of the difference in chemical behaviour.

A determination of the periods of the two isomers gives 18·6 ± 0·1 min and 62·0 ± 1·0 min.

THE existence of a difference in the chemical behaviour of nuclear isomers, as well as of the other isotopes produced by the (n,γ)-reaction has been disputed;[1–7] several papers,[8–12] however, seem to confirm the previous point of view of the authors of this paper.

To elucidate the problem, it seems interesting to investigate further the ^{81}Se isomers, and to see in this case whether the neutron energy influences the chemical behaviour of the isomers. The behaviour of these isomers when SeO_2 is irradiated has been studied in the solid state and in aqueous solution.

EXPERIMENTAL

1. *Irradiation*

Fast neutrons are produced by a (d,n) reaction of a 50–100-μA beam of deuterons of 11·5 MeV on a beryllium target in the Louvain cyclotron. The samples are protected by cadmium from thermal neutrons.

Slow neutrons are produced by slowing-down the fast neutrons in a 10 × 10 × 10-cm paraffin block, in the middle of which are placed the target materials without cadmium shield.

[1] J. CHIEN and J. E. WILLARD *J. Amer. chem. Soc.* **76,** 4735 (1954).
[2] F. S. ROWLAND and W. F. LIBBY *J. chem. Phys.* **21,** 1495 (1953).
[3] P. C. CAPRON and E. CRÈVECOEUR *Bull. III Congr. Nat. Sci. Brux.* **214** (1950).
[4] P. C. CAPRON and E. CRÈVECOEUR *J. Chim. phys.* **49,** 29 (1952).
[5] P. C. CAPRON and Y. OSHIMA *J. chem. Phys.* **20,** 1403 (1952).
[6] P. C. CAPRON and E. CRÈVECOEUR *J. chem. Phys.* **21,** 1843 (1953).
[7] R. H. SCHULER *J. Chem. Phys.* **22,** 2026 (1954).
[8] U. CROATTO, G. GIACOMELLO, and A. G. MADDOCK *Ric. Sci.* **22,** 265 (1952).
[9] M. MILMAN and P. F. D. SHAW *J. chem. Soc.* **412,** 2101 (1956).
[10] R. M. S. HALL and N. SUTIN *J. inorg. nucl. Chem.* **2,** 184 (1956).
[11] P. C. CAPRON and L. J. GILLY *J. Chim. phys.* **52,** 505 (1955).
[12] D. J. APERS and P. C. CAPRON *J. inorg. nucl. Chem.* **2,** 219 (1956).

The samples are irradiated for 10 min, giving the same average lifetime during irradiation for the two isomers. If T is the time of irradiation, according to the formula:

$$\theta = \frac{1 - \exp(-\lambda T)(\lambda T + 1)}{\lambda\{1 - \exp(-\lambda T)\}}$$

the average life θ is 4·7 min for the short-lived isomer and 4·9 min for the long-lived one. As these average lifetimes during irradiation are very nearly equal, one can be sure that the two isomers have the same probability of reaction in chemical changes following their creation.

2. *Treatment of the Samples*

The "Analar" SeO_2 furnished by Hopkins and Williams, London, is used without further purification. Indeed, as will be shown below, the presence of possible impurities does not invalidate the result that a difference in the chemical behaviour of the selenium isomers is found.

To study the behaviour of the two recoiling isomers, it is necessary to extract the selenium which has not recombined. DAUDEL[13] uses coprecipitation of the selenium by nickel dimethylglyoxime or by gum-lac. On the other hand, GUEST and EDWARDS[14] filter on sintered porcelain of minimum porosity which retains free selenium selectively. (For the purpose of simplicity, "free selenium" indicates the fraction of activity retained on the porcelain disc, regardless of whether it is in an atomic or ionic state.) GUEST and EDWARDS' method is to be preferred for its simplicity.

The extraction process is as follows:

(*a*) *For the solid state.* The SeO_2 samples, 4 cm² in area and 125 mg/cm² thick, are dissolved in 10 ml distilled water as soon as possible after the end of irradiation. They are then filtered on a 3 mm thick sintered porcelain disc (No. 4, minimum porosity: 5–10 microns). The residue is washed several times with distilled water: this yields the free selenium. This fraction will be referred to as "residue" selenium.

Ammonia is then added to the filtrate until alkaline. Finally, all the selenium anions are precipitated with $BaCl_2$ and filtered through a Buchner flask. This fraction will be referred to as "filtrate" selenium.

(*b*) *For the dissolved state.* One g SeO_2 is dissolved in 10 ml distilled water in a test tube before irradiation. Thereafter exactly the same treatment is followed as described above for the solid state.

When selenium oxide is irradiated in the solid state in the form of a 4 cm² detector, 125 mg/cm² thick, or in the dissolved state (1 g SeO_2 in 10 ml distilled water), the same ratio of the isomeric activities is obtained, as can be seen in Table 1. This means that the variation in the radiation geometry does not influence the results.

It may be pointed out that the ratios of the activities shown in Table 1 yield a ratio of the cross-sections which differs from that calculated from data given in the literature and summarized by the Bureau of Standards and the Argonne and Brookhaven National Laboratories.[15,16]

[13] R. DAUDEL *Compt. rend.* **213**, 479 (1941).
[14] H. GUEST and R. R. EDWARDS *Radiochemical Studies: The Fission Products.* Book 3. p. 1447 McGraw-Hill, New York (1951).
[15] *Nuclear Data* U.S. Department of Commerce, NBS, 499 (1950).
[16] *Neutron Cross-sections* McGraw-Hill, New York (1955).

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The accepted cross-sections are $0{\cdot}50 \pm 0{\cdot}10$ barn for the 17 min isomer and $0{\cdot}030 \pm 0{\cdot}010$ barn for the 57 min isomer, and give a ratio $R_\sigma = 17 \pm 7$.

TABLE 1.—PRELIMINARY EXPERIMENTS: RATIO OF TOTAL ACTIVITIES (INDUCED BY SLOW NEUTRONS)
(Counting ratio extrapolated to end of bombardment)

Solid			Solution		
C_0 (18 min)	C_0 (62 min)	R	C_0 (18 min)	C_0 (62 min)	R
32,982·5	2,078·4	15·9	36,422·1	2,482·4	14·7
60,353·9	4,062·1	14·9	57,826·7	3,824·0	15·1
29,008·7	2,073·1	14·0	34,403·2	2,116·5	16·2
47,155·4	4,496·4	10·5	42,926·7	3,533·4	12·1
50,577·7	3,065·1	16·5	50,736·1	3,224·9	15·7
48,381·2	3,421·1	14·1	19,913·6	1,235·0	16·1
24,551·4	2,039·4	12·0	35,983·8	2,373·5	15·2
$R_M = 14{\cdot}0 \pm 0{\cdot}7$			$R_M = 15{\cdot}0 \pm 0{\cdot}5$		

The experimental ratio $R_M = 15{\cdot}0$ resulting from the experiments related in this paper, becomes for an infinite irradiation time:

$$R_\infty = \frac{1 - \exp(-\lambda_1 T)}{1 - \exp(-\lambda_2 T)} R = 5{\cdot}1 \pm 0{\cdot}2$$

which yields a ratio of the cross-sections:

$$R_\sigma = \frac{\lambda_1}{\lambda_1 - \lambda_2} R_\infty + \frac{\lambda_2}{\lambda_1 - \lambda_2} = 7{\cdot}7 \pm 0{\cdot}2$$

In previous papers relating to the ratios of the neutron capture cross-sections of the isomeric pairs ^{69}Zn, ^{80}Br, and ^{81}Se,[17–20] it was shown that these ratios are very sensitive to the neutron energy.

The comparison between the R_σ given in the literature and the R_σ calculated here is difficult, because the energies of the neutrons are not the same; furthermore, one ignores the detailed experimental procedure and in particular one does not know whether the isomeric transition was taken into account in calculating the cross-sections.

The sintered porcleain disc is only radioactive on its upper side; this indicates a selective hold-back of the free selenium. It has also been verified that there is no remaining activity in the last wash-waters, nor on the walls of the flask used during experiments.

3. *Determination of the Activities*

The activities are measured by means of Tracerlab G.M. end-window counters (window thickness: 2·5 mg/cm²). They are automatically recorded by a photographic

[17] P. C. CAPRON and E. CRÈVECOEUR *C.R. XXVII Congr. Ind. Chim.* 222. Bruxelles (1954).
[18] P. C. CAPRON and E. CRÈVECOEUR *Acad. Roy. Belg. XL* (1955).
[19] P. C. CAPRON, E. CRÈVECOEUR, and M. G. FAES *J. chem. Phys.* **17**, 349 (1949).
[20] L. KATZ, L. PEASE, and H. MOODY *Canad. J. Phys.* **30**, 484 (1952).

camera every 3 min during one hour, after every 15 min during the two following hours, and then after every hour. This continuous recording of the decay curve allows corrections to be made for the resolving time of the apparatus and also serves to monitor the performance of the apparatus.

The activity at the end of the irradiation ($t = 0$) has been calculated by the integral method[6] applied over the interval $t = 180$ min to $t = 360$ min for the long-lived isomer, and $t = 33$ min and $t = 180$ min for the short-lived isomer. These activities have been corrected for background radiation and resolving time of the apparatus (which is of the order of 10^{-6} min.) These corrections amount in the worst case to less than 5 per cent.

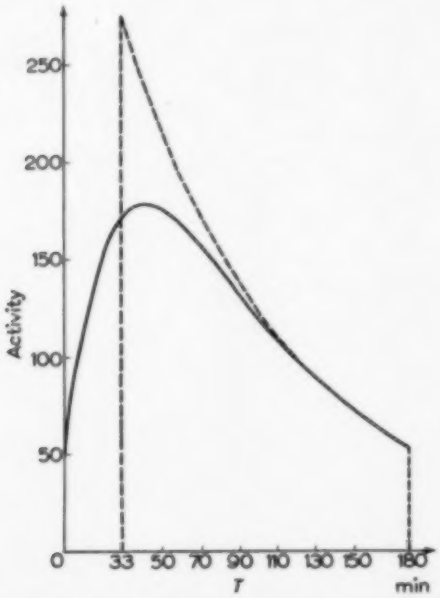

FIG. 1.—Growth of the (18 min) daughter isomer for 10 min irradiation.

The calculations are made starting from the thirty-third min for two reasons. First of all, some time was occupied by the post-irradiation manipulations (filtrations and precipitation). Also a delay was made necessary by the fact that the equilibrium between the Se (18 min) and its isomeric (62 min) parent must be reached.

The growth curve of the 18 min daughter for a 10 min irradiation can be derived from the formula:

$$C_t^T = n_0 \frac{\lambda_1}{\lambda_2 - \lambda_1} \left[\frac{\{1 - \exp(-\lambda_1 T)\} \exp(-\lambda_1 t)}{\lambda_1} - \frac{\{1 - \exp(-\lambda_2 T)\} \exp(-\lambda t)}{\lambda_2} \right]$$

with T = irradiation time; n_0 = number of active ^{81}Se (62 min) atoms produced per unit of time; t = time after irradiation; λ_1 = decay constant of the long-lived isomer, λ_2 = decay constant of the daughter isomer. As the curve shows, the equilibrium is nearly complete at the one hundred and twentieth min. But at this time the original (18 min) activity is too weak to measure accurately. The error introduced

by calculation from the thirty-third min can be determined as follows: the number of (62 min) active atoms which are not in equilibrium with their daughter isomer is given by the area included by the exponential decay line and the growth curve, and is expressed by:

$$n_0 \frac{\lambda_1}{\lambda_2 - \lambda_1} \cdot \frac{1 - \exp(-\lambda_2 T)}{\lambda_2} \int_{33}^{180} \exp(-\lambda_1 t)\, dt$$

This yields approximately 14 per cent for the interval 33–180 min, i.e. about 86 per cent of the (62 min) atoms have reached equilibrium.

If x = fraction which is in equilibrium, y = fraction which is not in equilibrium, N = number of counts which would have been recorded if no isomerization had occurred, and N' = number of counts actually recorded, then:

$$N = x \int_{t_1}^{t_2} \exp(-\lambda_1 t)\, dt + y \int_{t_1}^{t_2} \{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\}\, dt$$

and

$$N' = x \int_{t_1}^{t_2} \exp(-\lambda_1 t)\, dt + y \int_{t_1}^{t_2} \exp(-\lambda_1 t)\, dt$$

The physical meaning of these formulae is that, in resolving the complex decay curve, one subtracts too much 62 min activity in order to obtain the pure 18 min activity which is originally formed. This subtraction therefore attributes too little intensity to the primary 18 min activity when no correction is introduced, yielding ratios which are too small.

According to these formulae, a value of 86 per cent for the fraction of 62 min isomer reaching equilibrium causes an error of hardly 1 per cent in the activity ratio, which is quite negligible.

As a check, comparative calculations were made over the two intervals (33–180 min and 75–180 min). They give the same results within the statistical errors.

It might be objected that a difference in the activity ratios could result from the difference in the counting geometry of the free selenium samples and the $BaSeO_3$ samples. This is not so, since both isomers are measured by means of the same 1·38 MeV beta ray, the conversion electron occurring in the isomeric transition being too weak to be detected, as was shown by preliminary experiments. The absorption of the beta ray may be different in the two cases, but this cannot affect the ratios. It is not necessary to compare actual activities of the free selenium samples with the activities of $BaSeO_3$ samples to show the difference between slow- and fast-neutron irradiations.

RESULTS

The half-lives of the two isomers are first calculated by the least-squares method applied to the mean value of the decay curves of several experiments. The results in minutes are:

	Filtrate	Residue	Mean value
Shorter half-life	19·0 ± 0·1	18·2 ± 0·1	18·6 ± 0·1
Longer half-life	62·0 ± 0·6	62·0 ± 1·0	62·0 ± 1·0

These results are in agreement with those quoted, in most cases without indication of errors, in the literature: 17 min,[21 22] 18 min,[23] and 19 min,[24] 57 min,[22 24] and 58 min.[23]

The results are always expressed by the ratios of the activities at time $t = 0$. These ratios are more valuable than the retentions; they are indeed just as sensitive

TABLE 2.—SOLID STATE. SLOW NEUTRONS

Filtrate			Residue		
C_0 (18 min)	C_0 (62 min)	R	C_0 (18 min)	C_0 (62 min)	R
21,910·4	1,292·7	16·9	2,774·6	176·6	14·0
17,078·4	1,186·8	14·4	6,579·3	571·0	11·5
50,249·6	2,904·2	17·3	5,878·2	519·2	11·3
61,115·6	3,667·8	16·7	4,380·3	308·3	14·2
30,482·7	1,793·9	17·0	2,587·3	292·4	8·8
35,773·1	1,994·6	17·9	6,603·1	494·0	13·4
34,656·8	1,875·2	18·5	8,074·4	713·5	11·3
34,470·2	2,465·7	14·0	10,063·6	792·7	12·7
59,425·1	3,420·0	17·4			
51,389·3	3,233·4	15·9			
$R_M = 16·6 \pm 0·4$			$R_M = 12·2 \pm 0·6$		

TABLE 3.—SOLID STATE. FAST NEUTRONS

Filtrate			Residue		
C_0 (18 min)	C_0 (62 min)	R	C_0 (18 min)	C_0 (62 min)	R
1,130·1	205·1	5·5	1,253·0	308·1	4·1
1,535·2	282·0	5·4	562·6	99·2	5·6
1,409·4	232·5	6·0	2,202·3	355·4	6·2
3,032·4	627·8	4·8	3,734·0	884·0	4·2
2,458·0	487·1	5·0	729·6	210·8	3·5
1,094·7	239·8	4·6	1,590·8	503·4	3·2
2,597·8	705·1	3·7	1,502·6	366·5	4·1
871·1	207·4	4·2	1,796·2	416·8	4·3
$R_M = 4·9 \pm 0·3$			$R_M = 4·4 \pm 0·3$		

as the retentions. Furthermore, they have the advantage of being derived from one single experiment, while the retentions need the comparison of at least two experiments, which increases the possibility of experimental errors. Expression of the

[21] A. SUGARMAN *J. chem. Phys.* **15**, 703 (1947).
[22] G. T. SEABORG *Rev. mod. Phys.* **16**, 1 (1944).
[23] G. FRIEDLANDER and G. W. KENNEDY *Introduction to Radiochemistry* John Wiley, New York (1949).
[24] L. SEREN, H. N. FRIEDLANDER, and S. H. TURKEL *Phys. Rev.* **72**, 888 (1947).

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TABLE 4.—AQUEOUS SOLUTION. SLOW NEUTRONS

Filtrate			Residue		
C_0 (18 min)	C_0 (62 min)	R	C_0 (18 min)	C_0 (62 min)	R
11,255·1	687·7	16·3	21,219·3	1,393·3	15·2
25,000·0	1,377·4	18·1	28,610·3	1,964·7	14·6
26,211·9	1,879·1	13·9	45,913·2	3,344·0	13·7
21,664·1	1,623·6	13·4	31,556·2	2,243·2	14·0
6,843·1	506·5	13·5	33,602·9	2,129·1	15·8
24,881·8	1,647·8	15·1	31,629·8	1,737·9	18·2
16,996·4	1,061·2	16·0	9,260·3	611·2	15·2
7,275·0	465·0	15·6	20,972·8	1,150·0	18·2
3,916·9	274·7	14·2	13,360·8	950·0	14·0
18,564·6	1,381·0	13.4	18,246·2	1,644·1	10·8
13,638·1	863·4	15·7	6,362·2	443·5	14·3
$R_M = 15·1 \pm 0·4$			$R_M = 14·8 \pm 0·6$		

TABLE 5.—AQUEOUS SOLUTION. FAST NEUTRONS

Filtrate			Residue		
C_0 (18 min)	C_0 (62 min)	R*	C_0 (18 min)	C_0 (62 min)	R
2,337·0	368·9	6·3	3,218·0	554·2	5·8
2,569·9	374·1	6·9	5,476·5	973·1	5·6
1,185·1	139·1	8·5	4,815·9	1,134·5	4·2
3,716·2	339·4	10·9	2,239·9	367·2	6·1
3,272·2	505·8	6·5	3,418·4	567·2	6·0
1,685·4	165·2	10·2	5,817·8	969·5	6·0
4,353·1	645·6	6·7	791·7	159·2	5·0
4,228·1	375·4	11·2	385·4	83·9	4·6
715·9	94·2	7·6	4,143·4	737·4	5·6
$R_M = 8·3 \pm 0·6$			$R_M = 5·4 \pm 0·2$		

*Although some results have a rather large dispersion, none of them is eliminated by CHAUVENET's criterion.

TABLE 6.—RATIO OF THE ACTIVITIES: SUMMARY OF THE RESULTS

Neutrons	Solid		Aqueous solution	
	Residue	Filtrate	Residue	Filtrate
Slow	$12·2 \pm 0·6$	$16·6 \pm 0·4$	$14·8 \pm 0·6$	$15·1 \pm 0·4$
Fast	$4·4 \pm 0·3$	$4·9 \pm 0·3$	$5·4 \pm 0·2$	$8·3 \pm 0·6$

results in this way is quite common among European workers such as MADDOCK,[18] SHAW,[9] SUTIN,[10] and CAPRON. Our results are recorded in Tables 2–6. The errors given are the mean standard deviations "E," and are calculated from the experimental results. Consequently, in the case of the fast-neutron irradiation in the aqueous solution, and of the slow-neutron irradiation in the solid state, the chance that the differences observed are fortuitious is less than 1/369.

It may also be noted that in some series of experiments the statistical fluctuations seem rather large. A sufficient number of experiments have been done to take these fluctuations into account. They are inherent in this kind of experiment, as one can see in all papers treating the subject.[25,26]

DISCUSSION

I. Examination of Table 6 allows the statement: the chemical behaviour of the nuclear isomers of ^{81}Se varies as a function of the energy of the incident neutron and as a function of the physical state of the irradiated sample. This is in accordance with the effects found for the ^{80}Br isomers[11,12] and also with effects found for the isotopes 80 and 82 of bromine.[27]

II. This conclusion cannot be ascribed to a difference in the mean average lifetime of the two isomers during irradiation. Indeed, the time of irradiation is so chosen that the mean average lifetime during irradiation can be considered as equal for both isomers (4·7 and 4·9 min), so that each has an equal chance of reaction.

Neither could the difference in the activity ratios be ascribed to impurities even if these were present. Clearly, if there were no impurities the difference in activity ratios could only mean a difference in chemical behaviour of the two isomers with respect to reactions with the pure target material. If impurities were present with which the isomers could react, the difference in activity ratios still indicates that the isomers react differently.

III. The difference existing between the case of slow-neutron irradiations in the solid state and the case of fast-neutron irradiations in the solution state might possibly be based on different recoil energies or on different charges, both involving a different chemical behaviour of the two isomers. Furthermore, the recoil is shorter in the solid state than in the solution state. No satisfactory explanation can be advanced as yet.

IV. These data confirm earlier results with the bromine isomers and isotopes.[11,12,27] Thus, it seems that this phenomenon is not peculiar to bromine, but is inherent in different isomeric pairs and isotopes.

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They thank Dr. A. G. MADDOCK (Cambridge) and Dr. P. F. D. SHAW (Oxford) for most fruitful and encouraging discussion.

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[27] D. J. APERS, P. C. CAPRON, and L. J. GILLY *J. Chim. phys.* **4**, 314 (1957)

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NEUTRON IRRADIATION OF SOME CRYSTALLINE SALTS OF PHOSPHORIC, PHOSPHOROUS, AND HYPOPHOSPHOROUS ACIDS IN VACUUM*

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Abstract—The radioactive products obtained by the neutron plus gamma irradiation of phosphorus compounds depend upon the conditions of the irradiation and upon the nature of the compounds irradiated. In vacuum, where easily oxidized, neutron activation products such as elemental phosphorus or phosphine should be recoverable, the principal radioactive irradiation product of anhydrous Na_2HPO_4 was phosphate, which was accompanied by traces of phosphorus and several unidentified products. The principal radioactive irradiation products of anhydrous Na_2HPO_3 and NaH_2PO_2 were phosphite and hypophosphite accompanied by a little phosphate and phosphorus. Neither phosphine nor diphosphine was detected as an irradiation product of these salts. The principal neutron irradiation products of PH_3 were H_2 and radioactive PH_3 and P. As shown by analysis, most of the radioactive products were formed in chemically detectable quantities, but the specific activity of these products was greater than that of the irradiated substances themselves.

In vacuum, gamma rays alone scarcely altered Na_2HPO_4, but they converted Na_2HPO_3, NaH_2PO_2 and PH_3 into the same products formed by neutrons plus gamma rays.

In the reactor where the gamma rays accompanying the neutrons are very intense, the final neutron irradiation products of Na_2HPO_4, Na_2HPO_3, and NaH_2PO_2 in vacuum were the primary neutron activation products, the gamma-ray alteration products of these primary activation products, and the neutron activation products of the gamma-ray modifications of the original salts.

Slight alteration of the phosphate by neutrons plus gamma rays indicates that the dissipation of the nuclear energy after the absorption of a neutron does not disrupt the chemical bonds of the recoiling atoms in nearly all instances. The formation of similar products by gamma irradiation and by neutron plus gamma irradiation of phosphite and hypophosphite indicates that the gamma-induced reactions and the neutron-induced reactions have similar but not necessarily identical mechanisms.

WHEN pure crystalline compounds are irradiated with neutrons, some of the atoms that absorb the neutrons remain in their original chemical form even though the energy of the accompanying nuclear rearrangements is sufficient to rupture all their chemical bonds. Other similar atoms that absorb the neutrons are converted into a variety of chemical species depending upon the element, upon the compound irradiated, and upon the experimental conditions.[1–3]

In the case of crystalline, hydrated phosphates, ($NaH_2PO_4 \cdot H_2O$, $Na_2HPO_4 \cdot 12H_2O$, and $Na_3PO_4 \cdot 12H_2O$), bombarded in air with neutrons from a Ra-Be source, LIBBY[1] reported that some 30 to 50 per cent of the radioactive phosphorus atoms remained as phosphate. This conclusion was based upon the observation that about 30 to 50 per cent of the radioactive phosphorus was precipitated from solutions of the irradiated

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
[1] W. F. LIBBY *J. Amer. chem. Soc.* **62,** 1930 (1940).
[2] A. G. MADDOCK *Research* **2,** 556 (1949).
[3] J. G. A. FISKELL, W. A. DELONG, and W. F. OLIVER *Canad. J. Chem.* **30,** 9 (1952).

salts as magnesium ammonium phosphate. The chemical form of the unprecipitated phosphorus was not reported. With $Na_2HPO_3 \cdot 5H_2O$ irradiated in air, some 92 per cent of the radioactive phosphorus remained in a form oxidizable to phosphate with bromine, and this was presumed to be phosphite. With similar methods of analysis, ATEN[4] found that irradiation of $Na_2SO_4 \cdot 10H_2O$ produced radioactive phosphorus compounds with 91 per cent as phosphate and 9 per cent as an unidentified reduced form, presumably phosphite. Likewise, irradiation of $Na_2SO_3 \cdot 7H_2O$ produced radioactive phosphorus compounds with 40 per cent as phosphate and 60 per cent oxidizable to phosphate and presumed to be phosphite. THOMAS and NICHOLAS[5] found that irradiation of Na_2HPO_4 under unspecified conditions in the Harwell reactor yielded only 50 per cent of the activity as phosphate and the remainder in chemical species convertible to phosphate by treatment with concentrated nitric acid and 60 per cent perchloric acid.

After irradiation of dried monocalcium phosphate at the Chalk River Laboratories, FISKELL, DELONG, and OLIVER[3] reported 30 per cent of the phosphorus activity as phosphate, determined as the molybdate, 45 per cent as hypophosphate, determined as silver salt or as the bromine oxidation product precipitable with molybdate, and about 16 per cent (the difference between the silver-salt activity and the zinc-salt activity) attributed to pyrophosphate. Tricalcium phosphate yielded 38 per cent phosphate, 36 per cent hypophosphate, and 32 per cent metaphosphate, determined as the barium salt after demineralization in an Amberlite IR-100 column. FISKELL, DELONG, and OLIVER[3] did not find phosphine among the irradiation products of phosphates. They did, however, report a radioactive gas, presumably phosphine, among the irradiation products of calcium hypophosphite.

ATEN, VAN DER STRAATEN, and RIESEBOS[6] irradiated several crystalline phosphates with neutrons from the cyclotron (without specification of the irradiation conditions). They then separated the pyrophosphate, with carrier, as the zinc and cadmium salts which were hydrolysed to phosphate and estimated as magnesium ammonium phosphate, leaving a small amount of activity attributed to phosphite and hypophosphite. Phosphate was determined, with carrier, as the magnesium ammonium phosphate, leaving much residual activity attributed to phosphite plus hypophosphite. From the average of the results and with the two fractions of phosphite plus hypophosphite added together, the proportional distribution of the activity from the several irradiated compounds was:

Na_2HPO_4	PO_4,	0·23	P_2O_7, 0·25	$PO_3 + PO_2$, 0·53
$Na_2HPO_4 \cdot 2H_2O$	PO_4,	0·22	P_2O_7, 0·18	$PO_3 + PO_2$, 0·59
$Na_2HPO_4 \cdot 5H_2O$	PO_4,	0·12	P_2O_7, 0·07	$PO_3 + PO_2$, 0·82

A more comprehensive analysis of the neutron irradiation products of phosphate has been obtained by differential electrical migration in lactic acid solution stabilized with soft filter paper. With this electrochromatographic method of separation, the mixture of the radioactive, neutron irradiation products formed in air has been resolved without loss of any of the components. For example, NORRIS, SATO, and

[4] A. H. W. ATEN, JR. *Rec. trav. chim.* **61**, 467 (1942).
[5] W. D. E. THOMAS and D. J. D. NICHOLAS *Nature, Lond.* **163**, 719 (1949).
[6] A. H. W. ATEN, JR., H. VAN DER STRAATEN, and P. C. RIESEBOS *Science* **115**, 267 (1952).

STRAIN[7] observed that neutron irradiation of phosphates, including NaH_2PO_4, $CaHPO_4$, apatite and bone, followed by electrochromatographic analysis, yielded primarily radioactive phosphate plus several unidentified species of phosphorus compounds. The nature and the proportions of these products separated by electrical migration varied with the chemical form and the previous treatment of the phosphate that was irradiated. Electrochromatographic comparison of these neutron activation products with authentic phosphorus compounds by SATO, NORRIS, and STRAIN[8] indicated that the principal product was usually the substance that was irradiated. Hypophosphorus acid, which occurs among the minor radioactive products, migrated faster than phosphate. In illustrating the importance of differential migration methods of analysis to agriculture, STRAIN and SATO[9] showed that phosphite is also a neutron activation product of certain phosphorus compounds. The phosphite formed a migrating zone between the phosphate and the hypophosphite. Pyrophosphate, formed from some phosphorus compounds, migrated along with the hypophosphite, but with a little zinc salt in the lactic acid, the pyrophosphate precipitated at the starting point while the other acids of phosphorus migrated through the medium.

Utilization of the electrochromatographic method of analysis also revealed that complex condensed phosphates probably occur among the neutron-irradiated phosphorus compounds. SATO, KISIELESKI, NORRIS, and STRAIN[10] found that certain condensed phosphates migrate slower than phosphate. SATO and NORRIS[11] and SATO, NORRIS, KISIELESKI, SMETANA, and STRAIN[12] demonstrated that condensed phosphates similar to slowly migrating products formed in neutron-irradiated phosphate[7] arise from heating phosphate and from the gamma-ray irradiation of phosphate.

Most of the neutron irradiations of phosphate were carried out in air in nuclear reactors where the samples were exposed to a high intensity of gamma rays as well as to neutrons. Easily oxidizable irradiation products, such as phosphorus, phosphine, or diphosphine, might, therefore, have been converted into various oxidation products. Moreover, the gamma rays might produce chemical changes, such as condensation, before reaction of the phosphates with neutrons. They might also produce chemical changes of the primary neutron irradiation products. In addition to the primary neutron activation products, the final neutron irradiation products of phosphates might therefore contain oxidized primary neutron irradiation products, gamma irradiation products of the various oxidation products of the phosphates themselves, and neutron activation products of these gamma irradiation products.

In order to collect further information about the neutron activation products of phosphate and to gain a better insight into the mechanism of neutron reactions with chemical compounds, we have now irradiated anhydrous phosphate (Na_2HPO_4), phosphite (Na_2HPO_3), and hypophosphite (NaH_2PO_2) with gamma rays and with

[7] W. P. NORRIS, T. R. SATO, and H. H. STRAIN *Quarterly Report, Division of Biological and Medical Research* p. 69. Argonne National Laboratory, ANL-4745 (1951–1952).
[8] T. R. SATO, W. P. NORRIS, and H. H. STRAIN *Abstracts of papers* p. 43. 124th meeting Amer. Chem. Soc. Chicago (1953).
[9] H. H. STRAIN and T. R. SATO *A Conference on the Use of Isotopes in Agriculture* pp. 175–182. (Held January 1956). U.S. Atomic Energy Commission, TID-7512, Washington, D.C.
[10] T. R. SATO, W. E. KISIELESKI, W. P. NORRIS, and H. H. STRAIN *Anal. Chem.* **25**, 438 (1953).
[11] T. R. SATO and W. P. NORRIS *Quarterly Report, Division of Biological and Medical Research* p. 62. Argonne National Laboratory, ANL-5247 (1954).
[12] T. R. SATO, W. P. NORRIS, W. E. KISIELESKI, F. SMETANA, and H. H. STRAIN *Quarterly Report, Division of Biological and Medical Research* p. 83. Argonne National Laboratory, ANL-5576 (1956).

neutrons plus gamma rays. To prevent oxidation of the products, we have performed the irradiations in vacuum. We have removed the gaseous products and have analysed them with the mass spectrometer. We have separated the non-volatile products by electrochromatography, and we have compared these products with authentic preparations of various phosphorus compounds. We have also studied the effect of neutrons plus gamma rays and the effect of intense gamma rays alone upon phosphorus, upon phosphorus plus hydrogen, and upon phosphine. With all these phosphorus compounds, we have determined the chemical yields of the irradiation products as well as the radiochemical yields of the radioactive products.

EXPERIMENTAL

Materials for irradiation

Most of the salts for the irradiations were anhydrous, commercial preparations of disodium phosphate, disodium phosphite, and monosodium hypophosphite. The disodium phosphate was also prepared from phosphoric acid and sodium hydroxide. In preparation for the irradiations, 0·01 formula weight of each salt was placed in quartz tubes (2 × 5 cm) provided with a narrow neck (about 2 mm × 7 cm). These tubes were evacuated to a few microns pressure overnight, thus removing most sorbed water and all but minute traces of air. The tubes were then sealed, leaving a narrow neck several centimetres long, and a file mark was made about a centimetre from the sealed tip.

Phosphine was prepared by careful decomposition of phosphonium iodide with water. For this purpose, phosphorus-diphosphorus tetraiodide was prepared from phosphorus and iodine.[12] This tetraiodide was hydrolysed to phosphonium iodide and phosphoric acid, the former being isolated by sublimation. Phosphine was generated in vacuum by the careful addition of water to the phosphonium iodide. The gas was condensed with a bath of liquid nitrogen; any hydrogen was removed with the vacuum pump; and the phosphine was allowed to vaporize at the temperature of a carbon dioxide bath. A portion of this vaporized, dry phosphine (about 13 ml) was measured in a burette and transferred to an evacuated quartz tube of about 30 ml capacity. The connection to the tube was closed, and the phosphine was condensed with liquid nitrogen, while the quartz tube was sealed, a precaution that prevented decomposition of the phosphine by heat.

Red and yellow phosphorus were commercial preparations. Hydrogen, tested for purity with the mass spectroscope, was taken from a cylinder.

Irradiation

The salts and the phosphine were exposed to neutrons plus gamma rays in the vertical thimbles of the Argonne Reactor (CP-5), where the neutron flux was about 10^{13} neutrons per square cm per sec, where the gamma-ray radiation was roughly 500,000 r per min, and where the temperature was about 40 to 50°C. The energy from the absorbed gamma rays was, therefore, many times greater than the energy produced by recoil of the activated phosphorus atoms. Most exposures were for 48 hours. The irradiation turned the quartz tubes containing the salts a deep purple-blue, but it turned the tubes containing the phosphine red-blue, due apparently to a red deposit on the inside.

[12] J. B. WORK *Inorganic Syntheses* (Edited by W. C. FERNELIUS) Vol. II. p. 141. McGraw-Hill, New York (1946).

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The salts and the phosphine were exposed to gamma rays alone in the Argonne High-level Gamma-irradiation Facility, where the gamma rays are obtained from spent reactor-fuel elements. Exposures were made for 2 days and for 7 days, providing total gamma irradiation of 1 or 3×10^8 r. In 7 days, the gamma irradiation was only about one-fifth that received by samples placed in the reactor for 2 days ($1{\cdot}5 \times 10^9$ r). This gamma irradiation turned the quartz tubes containing the salts purple-blue, but those containing the phosphine a light brown-blue, due also to a thin red deposit on the inside.

Analysis

Gases. For analysis of the gases liberated by irradiation, the tubes containing the irradiated phosphorus compounds were placed in a larger tube, which was joined to a vacuum apparatus with a large standard-taper joint. This joint was sealed to a short tube about 1 cm in diameter, and this tube was sealed, in turn, at right angles, to the base of a vacuum-type stopcock. The hollow plug of the stopcock was provided with a sturdy eccentric glass projection extending into the base, and the exit tube was bent at right angles and sealed to a small tapered joint connecting horizontally with the vacuum line. By tilting the large tube and stopcock about the axis of this connection, the constricted, sealed tip of the tube containing the irradiated substances could be brought into the base of the stopcock. After the system was evacuated, a turn of the stopcock broke the constricted, sealed tip of the quartz tube and released the gases. These gases were transferred to a burette, measured, and then transferred to an evacuated glass tube provided with a stopcock and standard taper joint. They were analysed with the mass spectrometer, which provided very precise values for the molecular ratios. A special search was made for gases or vapours that might have been formed, as for example, hydrogen and diphosphine (P_2H_4, mol. wt. 66).[14] Analysis of pure phosphine revealed traces of hydrogen and of masses 33 and 32, the two latter corresponding to phosphine less one and two atoms of hydrogen, formed presumably by the dehydrogenation of phosphine itself in the mass spectroscope.

Electrochromatography. For separation of the non-volatile irradiation products, the irradiated salts were transferred to volumetric flasks (100 ml) and dissolved in water forming 0·1 formula weight solutions. The various oxyacids and any suspended free phosphorus contained in these solutions were separated by electrochromatography in a soft, acid-washed, commercial filter paper moistened with dilute acids. One migration procedure employing 0·1 M lactic acid was designed to facilitate semi-quantitative estimation of the irradiation products with a Geiger-Müller counter. A slightly different procedure employing acetic and phosphoric acids as well as lactic acid as the background electrolytic solutions was utilized to confirm the identity of the irradiation products located by radioautography of the electrochromatograms.

As noted already, zinc ions in the background electrolytic solution precipitate pyrophosphate near the starting point, while other oxyacids of phosphorus migrate through the medium.[9] A similar effect has been observed by the use of unwashed filter paper which contains magnesium and calcium salts. If this precipitation effect is to be avoided, special care must be exercised in washing and handling the filter paper.

For acid-leaching of the paper, Eaton-Dikeman filter paper (Grade 301, 0·03 inch

[14] E. C. Evers and E. H. Street, Jr. *J. Amer. chem. Soc.* **78**, 5726 (1956).

thick) in sheets about 2 ft wide and 6 ft long or in strips 3 in. wide and 6 ft long was encased in a polyethylene sheet and washed with M nitric acid by siphonage and downward percolation for 24 hours. The paper was then washed with distilled water for 3 or 4 days and dried in air on a table covered with clean polyethylene sheeting.

For regulation of temperature during the migrations, sheets or parallel strips of moistened paper were supported on a specially constructed, electrically insulated, flat, level, stainless-steel vessel through which water at nearly constant temperature could be circulated. For the construction of this combined support and temperature regulator, a stainless-steel pan 1 cm deep, 2 ft wide, and 5 ft long, was reinforced internally with parallel longitudinal stainless-steel I-bars 1 cm high. These I-bars extended to within 10 cm of each end of the pan and were spot-welded to the bottom at 10-cm intervals. The pan was covered with a stainless-steel sheet that was welded to the edge of the pan and spot-welded to the reinforcing bars at 10-cm intervals. An outlet and inlet tube were welded at one side near the ends. This flat vessel or tank was insulated electrically with a wrapping of two layers of polyethylene sheeting each 0·005 in. thick.

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For the differential electrical migrations, a strip of polyethylene sheeting 2 ft wide was placed on the insulated, water-cooled tank, and a wide sheet or parallel strips of the acid-washed paper were placed on the polyethylene. The paper was moistened with 0·1 M lactic acid solution, and the excess solution was allowed to drain into large plastic electrode vessels at the ends of the tank. These electrode vessels were prepared from blocks of polymerized solidified polystyrene foam 2 ft 6 in. long and 6 in. square that were hollowed out by narrow parallel cuts with a circular saw to produce a cavity 2 ft 3 in. long, 3 in. wide, and 3 in. deep. The moistened paper was blotted lightly with clean paper towels, and each end was dipped into about 3 litres of the lactic acid solution in each electrode vessel. The moist paper between the solutions in the electrode vessels (162 cm long) was covered with a sheet of polyethylene, and a siphon was used to level the liquid in the two vessels. This system was allowed to stand for about 6 hours. The polyethylene cover was removed momentarily, and the solutions (100 μl) of the mixtures were placed at separate marked points in a line about 10 cm from the end of the stainless-steel tank near the cathode. In the paper sheets, these starting spots were about 3 in. apart. In the narrow paper strips, one spot was placed on each strip. The paper was then covered again with the polyethylene, and d.c. electrical potential (about 800 V or 5 V per cm) was applied to the large graphite electrodes (nuclear reactor graphite, grade CS) for 24 to 30 hours (current, about 30 mA). After this electrolysis, the ends of the paper in the electrode vessels were cut off, the upper polyethylene sheet was removed, and the paper was allowed to dry in air. For purposes of identification, authentic preparations of the various phosphorus compounds were allowed to migrate alongside the irradiated samples.

The phosphorus compounds were also separated by electrical migration in 0·1 M acetic acid and in 0·05 M phosphoric acid, which were stabilized in wide sheets of acid-washed paper. These separations were made with the apparatus previously described.[10]

Detection of radioactive zones. For the location of radioactive phosphorus compounds separated by electrical migration and for their semiquantitative estimation, the paper was scanned with a shielded proportional Geiger-Müller counter fitted with a Mylar window 1 in. wide and 3 in. long and supplied with a 10 per cent mixture of

methane in argon. This counter, with a background of about 80 counts per min, was mounted horizontally on a brass plate $\frac{1}{2}$ in. thick, with an opening or window 1 in. wide and 3 in. long. This brass plate, with the counter tube attached above it, was mounted $\frac{1}{8}$ in. above two square brass bars which were parallel to the opening in the counter. These two brass bars were 1 in. thick, 1 in. apart, and $\frac{3}{8}$ in. above the paper to be scanned.

Wide paper to be scanned was cut into strips 3 in. wide and 3 ft long. These sections and the similar narrow strips employed for separate migrations were fastened to an aluminium strip, 3 in. wide and 3 ft long, with masking tape. The metal strip with the attached paper was then pulled under the counter, about 1·5 cm at a time, and the radioactivity was determined.

For the detection and location of the radioactive products separated by migration in 0·1 M acetic acid and in 0·05 M phosphoric acid, radioautographs were made with Kodak "No-screen" X-ray film. The separated substances were identified by reference to authentic preparations submitted to migration in the same sheet of filter paper.

Detection of non-radioactive zones. Non-radioactive phosphorus compounds separated by electrical migration in moist paper were located by neutron activation. For this activation, the paper was dried, placed on a sheet of polyethylene, and the two sheets were rolled together, providing a roll about 3 in. in diameter. This rolled paper was wrapped in aluminium foil and placed in the thermal column of the reactor for about a week at a neutron flux of approximately 10^{12} neutrons per sec. When removed from the reactor, the paper was permitted to "cool" for some 7 to 14 days to reduce the background of the paper itself. It was then unrolled, kept straight under iron rods for a day or two, and finally taped to the metal strips for measurement of the activity with the Geiger counter. Owing to the brittleness of the irradiated paper and to the unevenness of the paper strips under the counter, the background counts were not as uniform as those of paper in which radioactive substances had been separated.

Chemical analysis. For estimation of the chemical yields of the irradiation products, the principal components of the irradiated phosphorus compounds were determined by chemical methods. Phosphate was estimated photometrically as the phosphovanadomolybdate.[15] Phosphite was determined by oxidation with iodine in neutral solution.[16] Hypophosphite was ascertained by oxidation with ceric ions in acid solution.[17] Pyrophosphate was estimated by precipitation with tris(ethylenediamine)-cobalt(III) chloride at pH 7.[18] Phosphorus was not determined and may have interfered with the analysis for other substances.

RESULTS

Separation of mixtures. For the electrochromatographic comparisons and for chemical analysis, freshly prepared solutions of the salts were employed. To show that some common acids of phosphorus migrate at different rates, solutions of the inactive, non-irradiated salts were submitted to migration in separate strips of paper placed side by side on the support with their ends dipping into the same electrode vessels. The location of the zones, after migration, activation, and scanning, is shown in Fig. 1.

[15] C. J. Barton *Anal. Chem.* **20**, 1068 (1948).
[16] R. T. Jones and E. H. Swift *Anal. Chem.* **25**, 1272 (1953).
[17] D. N. Bernhart *Anal. Chem.* **26**, 1798 (1954).
[18] H. W. McCune and G. J. Arguette *Anal. Chem.* **27**, 401 (1955).

The separation of oxyacids of phosphorus from their mixtures by electromigration is shown by Fig. 2. Here the non-irradiated salts were mixed before migration. With a mixture containing pyrophosphate in addition to the three other acids, the hypophosphite and the pyrophosphate formed a single zone well separated from the

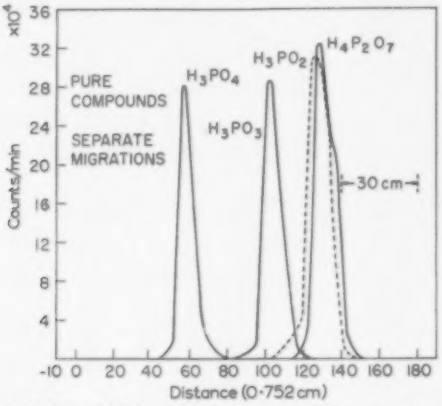

FIG. 1.—Zones of H_3PO_4, H_3PO_2, H_3PO_3, and $H_4P_2O_7$ after simultaneous migration in *separate*, parallel strips of filter paper. Located after activation with neutrons. Background solution, 0·1 M lactic acid. Time, 24 hours. D.C. potential, about 5 V per cm.

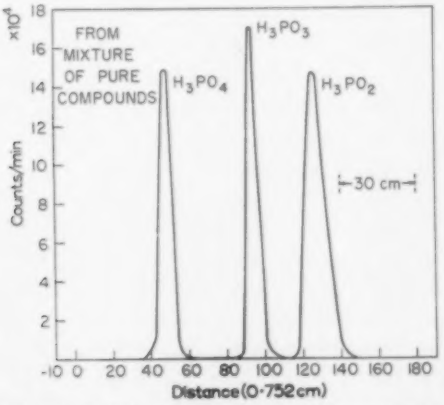

FIG. 2.—Zones of H_3PO_4, H_3PO_2, and H_3PO_3 separated by migration from a single spot in a strip of paper. Located after activation with neutrons. Background solution, 0·1 M lactic acid. Time, 24 hours. D.C. potential, about 5 V per cm.

phosphate and the phosphite. Similar results were also obtained with hypophosphate, which formed a zone migrating at nearly the same speed as pyrophosphate and hypophosphite.

Neutron-irradiated Na_2HPO_4. When the evacuated tubes containing neutron-irradiated Na_2HPO_4 were opened, only a trace of gas was observed, and this proved to be hydrogen (Table 1). Phosphine and diphosphine were not detected. When the irradiated salt was dissolved in water, a faint phosphorus-like odour was observed, and the solution had a barely perceptible yellow colour. Exposed to air, the solution became colourless after several days, but, treated with bromine water or hypochlorite, the solution was decolorized almost instantly.

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TABLE 1.—IRRADIATION PRODUCTS OF PHOSPHORUS COMPOUNDS
(Determinations independent of radioactivity)

Compounds	Irradiation	Products (mole per cent)					
		H_3PO_4	H_3PO_3	H_3PO_2	$H_4P_2O_7$	PH_3	H_2
Na_2HPO_4	n,(10^{13} n/s; 2d)	100	Not detected	Not detected	Not detected	Not detected	Trace
Na_2HPO_3	n,(10^{13} n/s; 2d)	2·5	89·0	4·0	Not detected	Not detected	$1·4 \times 10^{-4}$
NaH_2PO_2	n,(10^{13} n/s; 2d)	2·0	20·0	62·0	Not detected	Not detected	$3·8 \times 10^{-3}$
PH_3	n,(10^{13} n/s; 2d)	—	—	—	—	56·4	43·6
Na_2HPO_4	γ, (3×10^5 r)	100	Not detected	Not detected	Not detected	Not detected	Trace
Na_2HPO_3	γ_2, (3×10^6 r)	2·0	92·0	4·0	Not detected	Not detected	$1·6 \times 10^{-4}$
NaH_2PO_2	γ_2, (3×10^6 r)	0·4	9·0	80·0	Not detected	Not detected	$1·1 \times 10^{-3}$
PH_3	γ_2, (3×10^6 r)	—	—	—	—	94·9	5·1

A typical electrochromatogram of Na_2HPO_4 after exposure in the reactor for 2 days is reproduced as Fig. 3. Made in parallel and simultaneously with the migrations represented by Fig. 1, this separation provided a principal zone that must be attributed to phosphate. The proportions of small zones migrating slightly faster and slightly

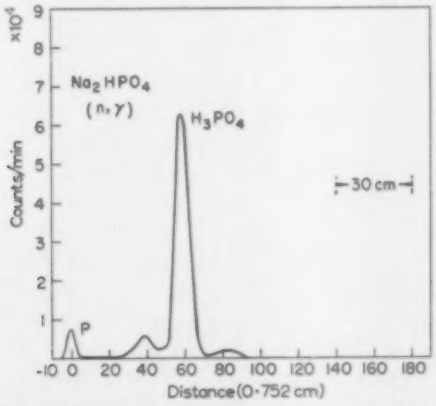

FIG. 3.—Radioactive products formed by neutron plus gamma irradiation of Na_2HPO_4 in vacuum and separated by electrical migration in a strip of paper as in Fig. 2. Zones identified by simultaneous migration of authentic phosphorus compounds which were located by neutron activation, as in Fig. 1.

slower than the phosphate zone varied significantly in different irradiation experiments. The zone remaining at the starting point was not found in solutions of the irradiated salt that had been allowed to stand in air for many days or that had been treated with bromine water.

Chemical analysis (Table 1) did not reveal a decrease in the phosphate content of

the neutron-irradiated salt. Neither did it reveal new substances produced from the phosphate.

Gamma-irradiated Na_2HPO_4. The Na_2HPO_4 exposed to gamma rays for 7 days provided only traces of gas, which proved to be hydrogen (Table 1). The solution of

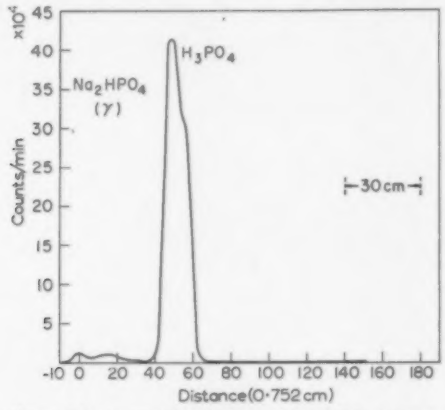

FIG. 4.—Products formed by gamma irradiation of Na_2HPO_4 in vacuum, separated by electrical migration in a strip of paper, and located after activation with neutrons, as in Fig. 1.

the gamma-irradiated salt was faintly yellow, and it was bleached with dilute bromine water. Separated by electrical migration in a strip of paper and then activated with neutrons, the gamma irradiation products yielded the curve shown in Fig. 4. By comparison with the location of phosphate ions in the same sheet of paper, the principal zone was unaltered phosphate. Traces of phosphorus or a phosphorus-like substance remained at the starting point. Chemical analysis did not reveal a detectable change in the phosphate (Table 1).

Neutron-irradiated Na_2HPO_3. The irradiated Na_2HPO_3 yielded a very small quantity of hydrogen, but no phosphine (Table 1). The salt had a phosphorus-like odour when dissolved in water, and it produced a pale yellow solution. This pale yellow solution was decolorized instantly with bromine water or with sodium hypochlorite. It was also decolorized slowly upon standing in air.

A typical electrochromatogram runs parallel and simultaneously with those shown in Figs. 1 and 3 is reproduced as Fig. 5. By comparison with Fig. 1 the principal zones in the order of their abundance were phosphite, hypophosphite, phosphate, phosphorus, an unidentified substance migrating faster than hypophosphite, and traces of two substances migrating slower and faster than phosphate. The zone at the starting point was not detectable in solutions that had been treated with bromine water.

Separate irradiations of Na_2HPO_3 in vacuum followed by electromigration in acetic acid solution revealed much activity migrating between the phosphate and the phosphite. By contrast, migration in 0·05 M phosphoric acid revealed little or no radioactive material in this region.

Chemical analysis revealed significant chemical changes of the irradiated Na_2HPO_3 (Table 1). Some 11 per cent of the phosphite had disappeared. More than half of this loss was accounted for as hypophosphite and as phosphate. Chemical tests failed to reveal any pyrophosphate (Table 1).

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The quartz tube in which the Na_2HPO_3 was irradiated was coated with a very thin layer of a yellow-red, radioactive deposit. This material was insoluble in water, acid, bases, and carbon disulphide. It dissolved rapidly in bromine water. Electrical

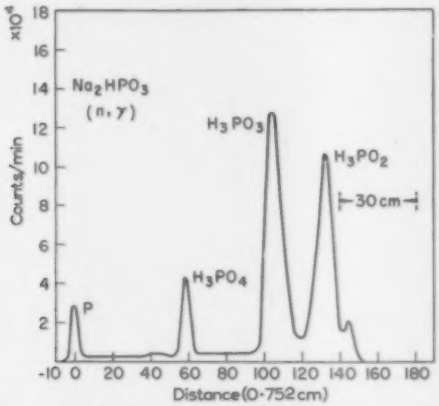

FIG. 5.—Radioactive products formed by neutron plus gamma irradiation of Na_2HPO_3 in vacuum and separated by electrical migration in a strip of paper, as in Fig. 2. Zones identified by simultaneous migration of authentic phosphorus compounds which were located by neutron activation, as in Fig. 1.

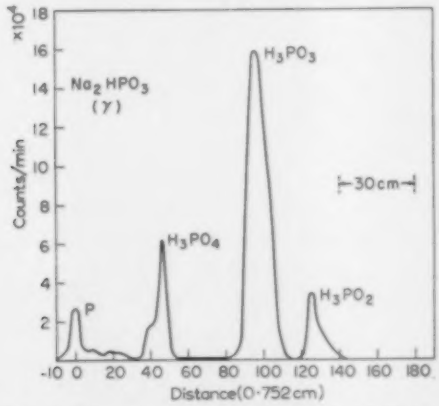

FIG. 6.—Products formed by gamma irradiation of Na_2HPO_3 in vacuum, separated by electrical migration in a strip of paper, and located after activation with neutrons, as in Fig. 1.

migration of this oxidized solution in paper moistened with lactic acid yielded two zones corresponding to phosphite and phosphate.

Gamma-irradiated Na_2HPO_3. The Na_2HPO_3 exposed to gamma rays for 7 days yielded a very small quantity of hydrogen. This irradiated salt formed a pale yellow solution that was bleached by bromine water.

An electrochromatogram formed in a strip of paper and activated with neutrons is shown in Fig. 6. From this curve, the most abundant products were phosphite, phosphate, hypophosphite, and phosphorus.

Chemical analysis (Table 1) indicated that about 8 per cent of the phosphite had undergone chemical alteration. About 6 per cent was accounted for as hypophosphite

and phosphate, the greatest proportion of the alteration products being hypophosphite, whereas the electrical migration indicated that phosphate was as abundant as hypophosphite.

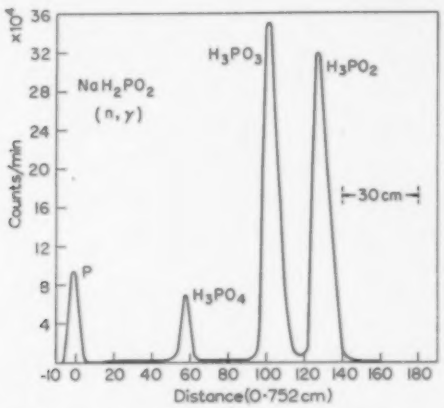

FIG. 7.—Radioactive products formed by neutron plus gamma irradiation of NaH_2PO_2 in vacuum and separated by electrical migration in a strip of paper, as in Fig. 2. Zones identified by simultaneous migration of authentic phosphorus compounds which were located by neutron activation, as in Fig. 1.

Neutron-irradiated NaH_2PO_2. This neutron-irradiated salt yielded a little hydrogen, but no phosphine or diphosphine (Table 1). Solutions were straw-coloured and were decolorized rapidly with bromine water or hypochlorite. They were decolorized slowly upon exposure to air.

An electrochromatogram prepared simultaneously with that shown in Fig. 1 is reproduced as Fig. 7. The principal radioactive irradiation products were phosphite, hypophosphite, phosphorus, and phosphate. The amount of activity in the hypophosphite zone was slightly less than that in the phosphite zone.

Chemical analysis (Table 1) showed that about 38 per cent of the hypophosphite had been altered by the neutron irradiation. About half of this was accounted for as phosphite, and a little more was present as phosphate. Pyrophosphate was not detected. Some 14 per cent of the total phosphorus, including the elemental phosphorus, was unaccounted for.

The quartz tube in which the NaH_2PO_2 was irradiated was coated with a thin, radioactive orange-red deposit. Washed with water, dissolved in bromine water, and submitted to electrical migration, this deposit yielded zones of phosphate and phosphite.

Gamma-irradiated NaH_2PO_2. The hypophosphite, after exposure to gamma rays for 7 days, resembled the neutron-irradiated product. It was sintered together and was light yellow in colour. It provided a trace of hydrogen, and it yielded a straw-coloured solution with a phosphorus-like odour. The solution was bleached rapidly with bromine and slowly upon exposure to air.

An electrochromatogram, prepared in 0·1 M lactic acid and activated with neutrons, provided the activity curve shown in Fig. 8. The most abundant substance was hypophosphite. Phosphite, phosphate, and phosphorus were present in significant quantities relative to that of the phosphite.

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Chemical analysis showed that about 20 per cent of the hypophosphite had been altered by the gamma irradiation. Nearly half of this altered hypophosphite was present as phosphite, with a little as phosphate (Table 1). About 10 per cent of the

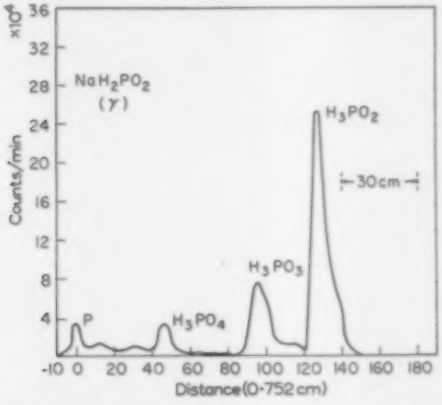

FIG. 8.—Products formed by gamma irradiation of NaH_2PO_2 in vacuum, separated by electrical migration in a strip of paper, and located after activation with neutrons, as in Fig. 1.

total phosphorus, including the elemental phosphorus, was unaccounted for by the chemical analysis.

As with the neutron irradiation, the walls of the quartz tube had a very thin coating of material insoluble in water but readily soluble in bromine water.

Neutron-irradiated PH_3. Irradiation of the phosphine, at about half an atmosphere pressure, with neutrons plus gamma rays for 2 days increased the volume of the gas about 25 per cent. In a typical irradiation, 12·2 ml PH_3 (n.t.p.) yielded 15·1 ml gas (n.t.p.). This gas, which was strongly radioactive, consisted entirely of phosphine and hydrogen (Table 1). Diphosphine was not detected. Because 56 per cent of the irradiated gas was phosphine, 8·5 ml or 70 per cent of the initial phosphine remained; 3·7 ml or 30 per cent was decomposed. Hydrogen comprised 6·6 ml of the irradiated product, slightly less than 1·8 times the 3·3 ml of the phosphine that was decomposed.

The quartz tube in which the PH_3 had been irradiated was coated with a red, radioactive deposit that had a phosphorus-like odour. This deposit was insoluble in water, acids, bases, and carbon disulphide. It was stable in air for many days. It dissolved readily in bromine water and in hypochlorite solution, yielding phosphate and phosphite.

Gamma-irradiated PH_3. The irradiation of the phosphine with gamma rays for 7 days produced only a slight increase in the volume of the gas. The only detectable, gaseous component, in addition to unaltered phosphine, was hydrogen (Table 1). A very thin orange-red deposit on the walls of the quartz tube resembled that obtained by neutron plus gamma irradiation of phosphine.

Neutron irradiation of P *plus* H_2. Irradiation of 0·01 formula weight of red phosphorus in hydrogen gas at 1 atmosphere pressure did not produce a radioactive gas. Examination of the gas with the mass spectroscope did not reveal detectable quantities of phosphine or diphosphine.

Irradiation of yellow phosphorus converted the yellow form into the red modification. Likewise, volatilization of the yellow form in vacuum by the use of heat

produced a deposit of the red form on the walls of the tube. As little as a milligram of the yellow phosphorus volatilized onto the walls of an evacuated quartz tube formed an opaque orange-red deposit.

DISCUSSION

The parallel migrations, shown in Fig. 1, indicate that phosphate and phosphite should be separable from each other and from hypophosphite or pyrophosphate. They also demonstrate that hypophosphite and pyrophosphite should not be separable from each other.

As no secondary zones were detected in the paper strips, large quantities of phosphorus-containing impurities could not have been present in the salts.

The results summarized in Fig. 2 demonstrate that mixtures of phosphate, phosphite, and hypophosphite are resolvable by electrochromatography and that the separated products may be identified by parallel migrations of authentic preparations, as indicated by Fig. 1. As mixtures of hypophosphite, pyrophosphate, and hypophosphate were not separable, none of these substances could have reacted rapidly in the mixture to form separable products. These different compounds that formed a single zone may be separated by migration under various conditions, as in solutions containing zinc ions, and by use of various selective reagents. These results illustrate that a basic rule of chromatography applies as well to electrochromatography. Preparations that form one migration zone may be identical, but they are not necessarily identical; preparations that form separate migration zones are different.

Table 1 summarizes the yields of the principal irradiation products without regard to their radioactivity. As the gamma irradiation accompanying the neutron bombardment was about five times the intensity of the irradiation by gamma rays alone, the yields of the alteration products resulting from neutron irradiation are much greater than those resulting from the gamma irradiation.

Figs. 3, 5, and 7 show the relative amounts of radioactivity found in various substances produced by the action of neutrons plus gamma rays on Na_2HPO_4, on Na_2HPO_3, and on NaH_2PO_2 respectively. These figures reveal the distribution of the radioactive phosphorus in the various products without regard to the quantity of the non-radioactive form of each substance present in the mixture.

Figs. 4, 6, and 8 indicate the substances formed by gamma irradiation of the phosphorus compounds. The individual products formed by gamma irradiation are similar to those formed by neutron irradiation. The relative quantities of these gamma irradiation products, revealed by neutron activation of the electrochromatograms, are in agreement with the quantities found by chemical analysis and reported in Table 1.

Fig. 3 shows that most of the radioactivity of neutron-irradiated Na_2HPO_4 was separable in the form of phosphate. Activity remaining at the starting point was due presumably to colloidal, elemental phosphorus, because this material exhibited the chemical properties of phosphorus. There is, of course, the possibility that traces of polyphosphates, some of which migrate slowly in lactic acid, may have remained at the starting point.[10,12] In acetic acid, by contrast, current investigations have shown that polyphosphates do not remain at the starting point, and with this acid, activity from the neutron irradiations did remain at the starting point, thus providing further indication of the presence of phosphorus. Two substances from the irradiated

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Na_2HPO_4 separated as minor zones at either side of the phosphate zone and have yet to be identified. It is significant that substances occupying the same relative position as these two substances have been found when phosphoric acid is heated or treated with gamma rays.[12] Fig. 3 also shows that pyrophosphate and hypophosphate were not formed in detectable quantities, because there was no activity in the region (100 to 160) where both of these substances would have separated. Chemical analysis (Table 1) showed that most of the phosphate remained unchanged. From the effect of gamma rays on phosphate (Fig. 4), the products formed by neutron irradiation may have been formed, in part at least, by the action of the attendant gamma rays on the phosphate itself. When it is recalled that the gamma irradiation producing the products shown in Fig. 4 was about one-fifth of that accompanying the neutron irradiation (Fig. 3), virtually all the radioactive products formed from phosphate may have arisen from the neutron activation of the gamma-irradiation products.

Fig. 5 shows that the neutron irradiation of Na_2HPO_3 produced relatively large amounts of a variety of active products. The amount of phosphorus was greater than that formed by neutron irradiation of phosphate. Pyrophosphate was not detectable by chemical tests; hence the zone labelled H_3PO_2 in Fig. 5 is probably free of pyrophosphate. Chemical analysis (Table 1) indicates that the chemical yields of the various products were less than the radioactive yields. Specifically only 4 per cent of the phosphite had been converted to hypophosphite, but nearly half of the radioactivity appeared in the hypophosphite. Even though 89 per cent of the phosphite remained unchanged, more than half of the activity appeared in the alteration products. From these facts, the neutron reactions with Na_2HPO_3 must have resulted in a preferential conversion of phosphite into other products.

The gamma-irradiation products of Na_2HPO_3, revealed by activation of the electrochromatogram (Fig. 6), were similar to those obtained by neutron irradiation. Here, too, phosphorus was present, but pyrophosphate was not detectable. Because of the formation of chemically detectable quantities of hypophosphite, phosphate, and phosphorus by gamma rays (Table 1 and Fig. 6), some of the radioactive, neutron irradiation products must have arisen by the action of neutrons upon these gamma transformation products of the original Na_2HPO_3.

Fig. 7 shows that neutron irradiation of NaH_2PO_2 also produced a variety of radioactive products like those formed from Na_2HPO_3. About half of the radioactivity of the neutron-irradiated NaH_2PO_2 occurred in the form of phosphite, whereas chemical analysis (Table 1) indicates that only 20 per cent of the phosphorus was present as hypophosphite. This higher specific activity of the phosphite indicates that the neutron activation leads to the conversion of hypophosphite into phosphite and other products as well as to the activation of hypophosphite alone.

Gamma irradiation of Na_2HPO_2 produced many of the same substances formed by the action of neutrons plus gamma rays as shown by Fig. 8. The formation of these products by gamma rays followed by activation with neutrons must occur in the reactor. Moreover, the activation of the gamma alteration products must be secondary to the primary neutron activation reaction, particularly in the early stages of the irradiation. As the neutron irradiation proceeds, however, the phosphite formed by attendant gamma irradiation will be activated with neutrons reforming hypophosphite as indicated by Fig. 5. Some hypophosphite will also be reformed by the gamma irradiation, as indicated by Fig. 6.

With Na_2HPO_3 and NaH_2PO_2, the specific activity of the irradiation products was greater than that of the salts exposed to the radiations. From this, the neutron irradiation must be very effective in altering the salts. Conversely, the attendant gamma irradiation followed by neutron activation of the products cannot account for formation of all the radioactive alteration products.

Upon irradiation of Na_2HPO_3 and NaH_2PO_2 in vacuum in the reactor, there are at least three courses by which the radioactive products may be formed. These are (1) the action of neutrons upon the pure salts, including chemical transformations of the salts due to nuclear rearrangements; (2) the action of gamma rays upon the neutron-activated products; (3) the action of gamma rays upon the original salts followed by neutron activation of these gamma irradiation products.

When the substances submitted to neutron irradiation undergo chemical changes, as with Na_2HPO_3 and NaH_2PO_2, the radioactive products that are formed may vary with the duration of the irradiation. In the reactor, the intensity of the gamma rays and the flux and speed of the neutrons vary with the location; hence, the neutron activation products and the proportions of these products should vary with the location in the reactor as well as with the duration of the exposure.

The irradiation of phosphine (Table 1) provides an indication that this substance is not an irradiation product of the salts of phosphate, phosphite, and hypophosphite. Neither neutron nor gamma irradiation of phosphine decomposed all this gas into a mixture of phosphorus and hydrogen. Had phosphine been formed from the salts, some of it should have remained and have been detectable with the mass spectroscope or as a radioactive gas.

The neutron plus gamma decomposition of phosphine led to the formation of phosphorus and hydrogen, not to the formation of detectable quantities of the lower hydrides of phosphorus such as diphosphine and $(PH)x$. Had lower hydrides of phosphine been formed there would have been no increase in the volume of the irradiated gas, but had the phosphine been decomposed to phosphorus and hydrogen there would have been an increase in volume due to liberated hydrogen and equal to 1·5 times the volume of the phosphine decomposed. Phosphine decomposed, 3·7 ml; hydrogen found, 6·6 ml, equivalent to $1{\cdot}8 \times 3{\cdot}7$ ml.

In view of its radioactivity, the phosphine may not have undergone extensive chemical disruption upon activation with neutrons. Instead, most of the decomposition may have been caused by the gamma rays. The regeneration of phosphine by the recombination of hydrogen and radioactive phosphorus seems unlikely, because irradiation of phosphorus and hydrogen did not produce phosphine as tested by radioactivity and by the mass spectroscope.

In the neutron irradiation experiments, there was no systematic relationship between the state of oxidation of the phosphorus in the salts and its state of oxidation in the radioactive products. Irradiation of phosphate by neutrons yielded primarily phosphate. Irradiation of phosphite produced principally the more reduced hypophosphite, whereas irradiation of hypophosphite produced principally the more oxidized phosphite. Analogous effects were obtained by the action of gamma rays alone.

Irradiation effects produced by gamma rays and by gamma rays plus neutrons resemble some of the effects produced by heat, but the several effects are not identical. With heat for example, Na_2HPO_4 yields principally pyrophosphate; Na_2HPO_3 and

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NaH_2PO_2 yield phosphine and phosphate. With heat there may well be an interconversion of Na_2HPO_3 and NaH_2PO_2, as is indicated for the action of gamma rays by Figs. 6 and 8 and also as is indicated for the action of neutrons by Figs. 5 and 7.

These irradiation experiments, as well as some carried out in air,[11] do not support the widely held view that a phosphorus atom receiving a neutron recoils with sufficient force upon the subsequent emission of the gamma ray to break the chemical bonds in nearly all instances. Indeed, with phosphate, most of the radioactive molecules remained in their original state of combination. With phosphite and hypophosphite about half of the active molecules remained in the original state of chemical combination, the remainder occurring in chemical species that could be formed by chemical rearrangements induced by gamma irradiation alone. With no compound, except phosphine, which is readily decomposed by gamma rays alone, was a high yield of phosphorus obtained. But even with phosphine, the neutron-irradiated gas was radioactive, indicating that it had not decomposed upon the absorption of a neutron by the phosphorus atom. With all these substances, the dissipation of the recoil nuclear energy accelerated those reactions which were promoted readily by irradiation with gamma rays alone.

The remarkable resistance of Na_2HPO_4 to irradiation in vacuum (Figs. 3 and 4) stands in sharp contrast to the earlier results, which indicate that irradiation in air yields various products.[1-12] Some of our current investigations now indicate that the formation of several products by irradiation of phosphates in air may be attributed to several distinct effects. At least three of these effects are: the action of neutrons and gamma rays upon phosphate followed by oxidation of the dissociation products, the action of gamma rays and oxygen upon the phosphate with formation of condensation products and subsequent activation of these products, and the use of non-specific chemical methods for the determination of the various activation products formed in air. These aspects of the neutron activation of other phosphorus compounds are being investigated.

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INFRA-RED SPECTRA OF INORGANIC SOLIDS—II

OXIDES, NITRIDES, CARBIDES, AND BORIDES

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Abstract—A series of oxide, nitride, carbide, and boride samples were scanned in the rock-salt region of the infra-red. The KBr disk technique was employed for the examination. The spectra show certain characteristic bands for each of the sets of compounds studied. Changes in band position for the major bands were noted with changes in mass for a number of the samples.

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A CONTINUATION of the study in the use of infra-red absorption spectra for identification purposes in inorganic chemistry[1] included an examination of some inorganic oxides, nitrides, carbides, and borides. In the article by MILLER and WILKINS[2] and also that of HUNT, WISHERD, and BONHAM,[3] a rather extensive number of infra-red patterns for inorganic substances were listed. However, MILLER's publication included the spectra of only one nitride sample and of three oxide samples, while HUNT's publication included only one spectrum of an oxide sample. In connection with other work that involved the study of some of the physical properties of the oxides nitrides, borides, and carbides, samples of Li_3N, Cu_3N, BN, AlN, CrN, Mg_3N_2, Zn_3N_2, B_2O_3, Al_2O_3, Ga_2O_3, Cr_2O_3, B_4C, SiC, Mo_2B, ZrB_2, and TiB_2 were available. Their infra-red spectra from 2 to 16 microns were determined and then examined for possible relationships.

EXPERIMENTAL

High-purity compounds were used. The two aluminium compounds were greater than 99·9 per cent pure. The procedure employed for the infra-red examination was that described by SCHIEDT and REINWEIN[4] and by STIMSON and O'DONNELL:[5] the KBr disk method. No special precautions were found to be necessary in the preparations. A disk which was 1 mm thick and 12 mm in diameter was produced from the operation. The disk was then scanned from 2 to 16 microns with the Baird Associates Model B infra-red spectrophotometer.

RESULTS

The infra-red spectra of Li_3N, BN, Mg_3N_2, AlN, Cu_3N, Zn_3N_2, B_2O_3, Al_2O_3, Ga_2O_3, Cr_2O_3, B_4C, and SiC are reproduced in Fig. 1 and wavelength positions of band centres are given in Table 1. The spectra generally showed water bands at 2·9 and 6·1 microns unless a large amount of energy scattering occurred or strong intensity bands appeared near these two wavelength positions. For both cases, the absorption bands for water were either considerably reduced in intensity or completely eliminated. The results of the spectral study showed: (1) characteristic bands

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[2] F. A. MILLER, and C. H. WILKINS *Anal. Chem.* **24**, 1253 (1952).
[3] J. M. HUNT, M. P. WISHERD, and L. C. BONHAM *Anal. Chem.* **22**, 1478 (1950).
[4] U. SCHIEDT and H. REINWEIN *Z. Naturf.* **76**, 270 (1952).
[5] M. M. STIMSON and J. O'DONNELL *J. Amer. chem. Soc.* **74**, 1805 (1952).

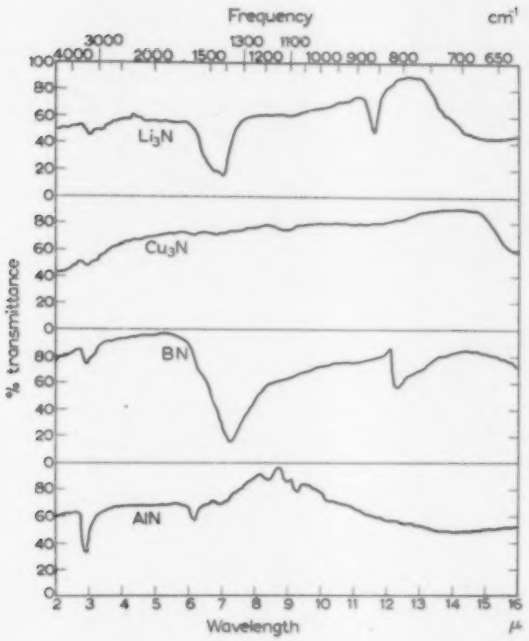
Frequency cm⁻¹
3000
1300 1100
4000 2000 1500 1200 1000 900 800 700 650
Li3N
Cu3N
BN
AlN
% transmittance
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Wavelength μ

FIG. 1(a)

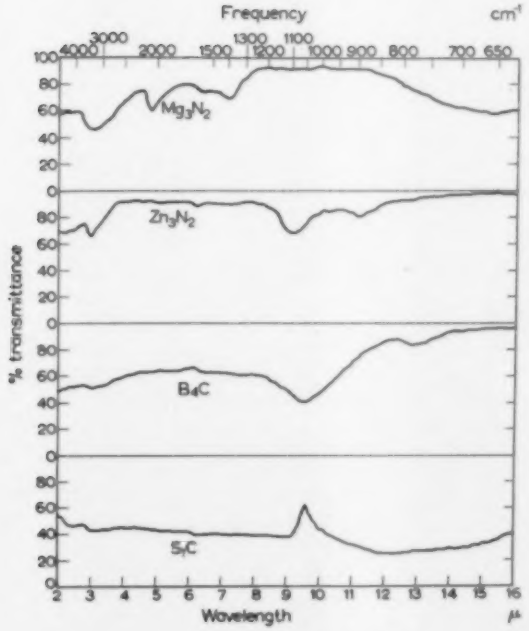
Frequency cm⁻¹
3000
1300 1100
4000 2000 1500 1200 1000 900 800 700 650
Mg3N2
Zn3N2
B4C
SiC
% transmittance
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
Wavelength μ

FIG. 1(b)

for most of the nitride samples, (2) a progressive shift of the strong intensity bands with changes of mass for most of the nitride samples, (3) characteristic bands for all of the oxide samples, (4) a regular shift of the strong intensity bands with changes

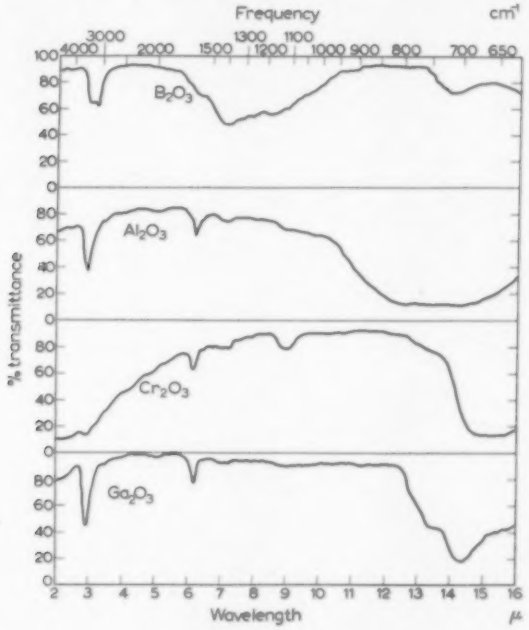

FIG. 1(c)

of mass between classes of oxide compounds, (5) a characteristic band for the two carbides studied and an observed band shift towards longer wavelengths with an increase of mass.

TABLE 1.—BAND CENTRES OF ABSORPTION BANDS

Name	Crystal structure[6]	Absorption bands (wavelengths in microns)
Li_3N	hexagonal	6·8 (*sh*) 7·0 (*s*) 11·6 (*m*) 15·2 (*m*)
Cu_3N	cubic	16·0 (*s*)
BN	hexagonal	7·28 (*s*) 12·3 (*m*)
AlN	hexagonal	8·45 (*w*) 9·46 (*w*) 14·0 (*m*)
Mg_3N_2	cubic	4·8 (*m*) 7·1 (*m*) 15·2 (*m*)
Zn_3N_2	cubic	9·1 (*m*) 11·15 (*w*)
B_2O_3	hexagonal	7·12 (*s*) 8·4 (*m*) 14·05 (*m*)
Cr_2O_3	rhombohedral	9·0 (*w*) 15·2 (*s*)
Ga_2O_3	rhombohedral	13·5 (*m*) 14·35 (*s*)
Al_2O_3	rhombohedral	13·5 (*s*)
B_4C	rhombohedral	9·5 (*m*) 12·9 (*w*)
SiC	hexagonal	12·0 (*m*)
Mo_2B	tetragonal	7·2 (*w*)

sh = shoulder; *s* = strong; *m* = medium; *w* = weak

DISCUSSION

The spectra of the nitride samples showed two strong intensity bands for all of the samples except for the copper and chromium nitrides. For the Cu_3N sample, only one band was observed, and this band appeared around 16·0 microns. Because the band appeared at the long-wavelength limit of the rock-salt region of scan, the actual band centre was not determined. For the CrN sample, no bands were observed in the rock-salt region. The remaining samples showed a regular shift toward longer wavelengths of the strong absorption bands with increase of mass.

A shift towards longer wavelengths was observed for bands of Li_3N, BN, and AlN, as predicted. A similar shift was observed in the absorption bands of Mg_3N_2 and Zn_3N_2, but a comparison between the first set of nitride samples and the second set did not follow the predictions of the mass effect. Since there is a crystal structure[6] difference between the two sets of nitride samples (Table 1), a change in position of the absorption bands which cannot be predicted from mass effect alone is to be expected.

Table 1 lists the crystal structure for the different compounds studied. In the different crystal structures, the environments and the distances between the oscillating atoms are changed and the variation of crystal structure is shown by differences in the force constants for the vibrations. With a change in force constants, the position of the absorption bands is shifted, since the frequency of vibration is directly related to the force constant.

The positions of the absorption bands for the BN sample are the same as observed by MILLER.[2] It is interesting to note that the spectrum of Li_3N appeared almost identical to that for Li_2CO_3. A spectrum of Li_2CO_3 is included in the list of spectra that were reproduced by MILLER.[2] It appears that the strong intensity bands of the metal nitrides which were scanned in the rock-salt region of the infra-red can be attributed to a metal-nitrogen vibration. This band assignment seems probable because of the mass influences which caused a shift of band positions.

The spectra of the oxide samples which were examined as well as the three oxide samples which were reported in the literature show characteristic absorption bands. The spectrum of Fe_2O_3 was reported by HUNT,[3] and the spectra of As_2O_3 and Sb_2O_3 were given by MILLER.[2] At least one strong absorption band was observed in the rock-salt region of the infra-red for each of the different oxide samples investigated. This band was shifted to longer wavelengths with increase of mass in the series B_2O_3, Al_2O_3, and Ga_2O_3, as predicted by the mass effect. Between the As_2O_3 and Sb_2O_3 samples, a shift in band position from 12·45 microns to 13·5 microns was observed in the direction predicted by the mass effect. The difference in location of band position between the two sets of oxide samples is attributed to differences in the force constants for the oscillating atoms. Differences in electronegativities between the two sets of oxide samples would effect the force constants, as indicated by GORDY's rule.[7] Thus, the strong intensity vibration band observed for each of the oxide samples is probably a metal-oxygen vibration.

It is interesting to note that the band shift for the main band between the BN and AlN samples was of the same order of magnitude as that for the B_2O_3 and Al_2O_3 samples: from 7·28 microns to 14·0 microns for the nitride samples and from 7·12

[6] R. W. G. WYCKOFF *Crystal Structure* Vol. I. Interscience, New York (1951).
[7] W. GORDY *J. chem. Phys.* **14**, 305 (1946).

microns to 13·5 microns for the oxide samples. The direction of shifts was expected from the mass effect. For the carbide samples a smaller band shift from 9·5 to 12·0 microns was noted between the B_4C and the SiC compounds. The smaller magnitude in band shift between these two compounds might be attributed at least in part to differences in crystal structure.[6]

Of the three boride samples investigated (Mo_2B, ZrB_2, TiB_2), only the Mo_2B sample showed any absorption bands. Even the principal band for this sample was very weak and broad.

Acknowledgements—We wish to thank SHELDON COHEN for preparing most of the nitride samples, the Carborundum Company for supplying the carbide samples and the boride samples, the Aluminum Company of America for supplying the AlN sample, the General Chemical Company for supplying the Al_2O_3 sample, BENNY BECK for supplying the Ga_2O_3 sample, and R. SIME for supplying the B_2O_3 sample.

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OBSERVATIONS ON SOME POTENTIALLY ASYMMETRIC GALLIUM(III) COMPOUNDS[1]

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Abstract—Attempts to resolve the potentially asymmetric tris(oxalato)gallate(III) ion by fractional crystallization, precipitation, or extraction techniques involving its salts with L-strychnine, L-quinine, D-cinchonine, and D-tris(ethylenediamine)-cobalt(III) have been unsuccessful. Inasmuch as the tris(oxalato)-gallate(III) ion in aqueous solution gives immediate precipitation of calcium oxalate with calcium ion and undergoes essentially instantaneous exchange with oxalate ion containing carbon-14, it is concluded that the ion is probably too unstable to retain asymmetry long enough to permit resolution. Negative results have been obtained in attempts to resolve the ethylenediaminetetraacetatoaquogallate(III) ion by fractional extraction of its L-brucine salt. Tris(ethylenediamine)cobalt(III) ion has been found to precipitate the tris(oxalato)gallate(III) ion quantitatively without precipitating oxalate ion.

THE successful partial resolution of the tris(oxalato)germanate(IV) ion[2] suggests a possible parallel with the very similar tris(oxalato)gallate(III) ion. NEOGI and DUTT[3] have reported resolution of this species by fractional extraction of the solid L-strychnine diastereoisomer. However, DWYER and SARGESON,[4] in work carried out approximately concurrently with but entirely independently of the present investigation, were unable to confirm this observation. The same negative result was obtained in this investigation, both with alkaloid and D-tris(ethylenediamine)cobalt(III) salts of the tris(oxalato)gallate(III) ion. Furthermore, the exchange of bound oxalate with free oxalate in solution was shown to be essentially instantaneous, suggesting that resolution by any technique involving aqueous systems is highly improbable.[5]

Another possibility is the 1 : 1-chelate of gallium(III) with ethylenediaminetetraacetic acid (H_4 enta). This species is potentially asymmetric regardless of whether the chelating agent is quinquedentate or sexadentate,[6] and its rather large formation constant ($\log_{10} K = 20{\cdot}27$)[7] suggests sufficient stability for maintenance of this asymmetry in solution. However, no resolution of this ion has been obtained by fractional extraction of its L-brucine salt.

EXPERIMENTAL

Materials and apparatus

The gallium compounds were synthesized directly or indirectly from spectroscopically pure gallium metal obtained from the Eagle-Picher Company. Oxalic acid-1,2,^{14}C was purchased from the Isotopes Specialty Company. Other chemicals

[1] Based upon a portion of the doctoral dissertation of E. H. GRAHN, University of Illinois (1955).
[2] T. MOELLER and N. C. NIELSEN *J. Amer. chem. Soc.* **75**, 5106 (1953).
[3] P. NEOGI and N. K. DUTT *J. Indian chem. Soc.* **15**, 83 (1938).
[4] F. P. DWYER and A. M. SARGESON *J. phys. Chem.* **60**, 1331 (1956).
[5] F. A. LONG *J. Amer. chem. Soc.* **61**, 570 (1939); **63**, 1353 (1941).
[6] T. MOELLER, F. A. J. MOSS, and R. H. MARSHALL *Ibid.* **77**, 3182 (1955).
[7] G. SCHWARZENBACH, R. GUT, and G. ANDEREGG *Helv. chim. Acta* **37**, 937 (1954).

were of reagent quality and were used without further purification. All optical rotation studies were made with a Schmidt and Haensch polarimeter or with a Hilger standard polarimeter, using sodium-D light. Ten readings, none of which deviated from the average by more than $\pm 0{\cdot}004°$, were taken for each sample. All countings of ^{14}C samples were made with a model D46A "Q Gas" flow-counter and a model 172 "Ultrascalar", both manufactured by the Nuclear Instrument and Chemical Corporation.

Preparation of ammonium tris(oxalato)gallate(III)

The procedure employed was that of NEOGI and DUTT,[3] using gallium(III) perchlorate 6-hydrate which had been prepared from the metal as outlined by FOSTER[8] (Found: Ga (from Ga_2O_3 residue), 18·16; C, 18·31; H, 3·45; N, 10·49. Calc. for $(NH_4)_3[Ga(C_2O_4)_3]$: Ga, 17·97; C, 18·58; H, 3·12; N, 10·83).

Preparation and attempted resolution of alkaloid salts of tris(oxalato)gallate(III) *ion*

The L-strychnine salt was prepared from the ammonium salt by the method of NEOGI and DUTT.[3] Both the L-quinine and D-cinchonine salts were prepared similarly. All salts were glassy solids which were appreciably hygroscopic, only slightly soluble in water, and very soluble in ethanol (Found: Ga (from residue), 4·86; C, 61·03; H, 5·57; N, 6·57. Calc. for $(C_{21}H_{22}O_2N_2H)_3[Ga(C_2O_4)_3]$ (strychnine): Ga, 5·20; C, 61·84; H, 5·19; N, 6·27) (Found: Ga (from residue), 4·94; C, 60·07; H, 5·89; N, 6·57. Calc. for $(C_{20}H_{24}O_2N_2H)_3[Ga(C_2O_4)_3]$ (quinine): Ga, 5·23; C, 60·51; H, 5·77; N, 6·42) (Found: Ga (from residue), 5·47; C, 61·52; H, 6·10; N, 6·96. Calc. for $(C_{19}H_{22}ON_2H)_3$-$[Ga(C_2O_4)_3]$ (cinchonine): Ga, 5·72; C, 62·02; H, 5·70; N, 6·89).

Resolutions were attempted by fractional crystallization, fractional extraction, and fractional precipitation techniques. Crystallizations were effected by dissolving the salts in ethanol-water mixtures, evaporating to crystallization at room temperature under a jet of dry air, and repeating the evaporation several times on the mother liquors. Extractions were carried out with water at room temperature, as outlined by NEOGI and DUTT.[3] Precipitations were effected by adding successive fractional equivalents of solutions of the alkaloid salts to solutions containing one equivalent of ammonium tris(oxalato)gallate(III). Optical rotations were observed on each fraction by dissolving the sample in 1 : 1-ethanol-water and measuring immediately in the polarimeter without removing the alkaloid.

Preparation and attempted resolution of D-*tris(ethylenediamine)cobalt*(III) *tris-(oxalato)gallate*(III)

Racemic tris(ethylenediamine)cobalt(III) bromide was prepared by a modification of the procedure of WORK,[9] and the D-isomer was obtained as outlined by WERNER[10] and by BUSCH.[11] Preliminary studies showed that the tris(ethylenediamine)cobalt(III) ion and the tris(oxalato)gallate(III) ion react quantitatively to give a yellowish-orange crystalline product, which is insoluble in hot or cold water, ethanol, ethyl ether, benzene, carbon tetrachloride, or chloroform, but soluble in

[8] L. S. FOSTER *Inorg. Synth.* **2**, 26 (1946).
[9] J. B. WORK *Inorg. Synth.* **2**, 221 (1946).
[10] A. WERNER *Ber. dtsch. chem. Ges.* **45**, 121 (1912).
[11] D. H. BUSCH *J. Amer. chem. Soc.* **77**, 2747 (1955).

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6 M nitric acid (Found: Ga + Co — (from $Ga_2O_3 + Co_3O_4$ residue), 22·01; C, 25·15; H, 4·22; N, 14·67. Calc. for $[Co(C_2H_8N_2)_3][Ga(C_2O_4)_3]$: Ga + Co, 22·45; C, 25·34; H, 3·99; N, 14·57).

Thus, the only technique available for potential resolution is fractional precipitation of the gallate species. The following procedure was employed: A solution of 0·5000 g of ammonium tris(oxalato)gallate(III) (0·00129 mole) in 25 ml of cold water was stirred vigorously and treated with a solution of 0·0619 g of D-tris(ethylenediamine)cobalt(III) bromide (0·000129 mole, or one-tenth the equivalent quantity) in a minimum volume of water. The precipitate was removed, and the solution containing the unreacted gallium chelate was observed with the polarimeter. The precipitation was repeated, using 20 per cent of the equivalent of the cobalt complex and the filtrate again observed with the polarimeter.

Radioactive exchange studies with ammonium tris(oxalato)gallate(III)

Inasmuch as calcium ion precipitates calcium oxalate when added to solutions of ammonium tris(oxalato)gallate(III),[1] it cannot be used to remove oxalate ion which has been equilibrated with the oxalato complex in exchange studies.[5] However, the tris(ethylenediamine)cobalt(III) ion can be used to remove the tris(oxalato)gallate(III) ion, since it does not form a precipitate with either the oxalate ion or oxalic acid.

For exchange studies, 0·5 mc of oxalic acid-1,2,^{14}C was dissolved in 10 ml of water to give a stock solution, 1 gamma of which had an activity of 1850 disintegrations per sec. Just prior to the equilibrium study, 200 gammas of this solution was pipetted into 100 ml of a 0·028 M ammonium oxalate solution. Other solutions employed were 0·028 M ammonium tris(oxalato)gallate(III) and 0·014 M racemic tris(ethylenediamine)cobalt(III) chloride.[9] All solutions were prepared by direct weighing.

20 ml of the ammonium tris(oxalato)gallate(III) solution was pipetted into a dry flask, and 20 ml of the radioactive ammonium oxalate solution was added. The solutions were mixed quickly at room temperature and a 5 ml aliquot was withdrawn immediately (*c.* 1 min elapsed time) and added to an excess (7 ml) of the tris(ethylenediamine)cobalt(III) chloride solution. This sample was considered withdrawn at zero time. Similarly, after 10, 20, 30, 45, 60, and 90 min intervals, other 5 ml aliquots were withdrawn and precipitated similarly. Each precipitate was removed by filtration through a stainless-steel Gooch crucible, washed with water and ethanol, and air-dried. The samples were transferred to aluminium counting pans and their activities measured. In another series, the time-intervals were 10, 20, 35, 50, 80, and 1200 min.

Preparation of ethylenediaminetetra-acetatogallic(III) *acid* L-*hydrate*

This compound was prepared by treating hydrous gallium(III) hydroxide with ethylenediaminetetra-acetic acid in a 1 : 1-mole ratio by an adaptation of the procedure of Moss.[12] Evaporation of the resulting solution gave the product as a hygroscopic, water-soluble glassy mass, which could not be recrystallized. The compound is stable in aqueous solutions below pH 4, but yields the hydroxide above this pH (Found: Ga (from residue), 19·50; C, 32·13; H, 4·22; N, 7·14. Calc. for $H[Ga(C_{10}H_{12}O_8N_2)(H_2O)]$: Ga, 18·50; C, 31·86; H, 4·01; N, 7·43).

[12] F. A. J. Moss Doctoral Dissertation, University of Illinois (1952).

Attempted resolution of ethylenediaminetetraacetatoaquogallate(III) ion

A suspension of 0·620 g of L-brucine 4-hydrate (0·00133 mole) in 35 ml of water containing 0·500 g of ethylenediaminetetraacetatogallic(III) acid 1-hydrate (0·00133 mole) was warmed and stirred until the solid dissolved. The solution was cooled, filtered, evaporated to a small volume, and placed in a vacuum desiccator to effect crystallization. The hygroscopic product was soluble in water, but not in ethanol (Found: Ga (from residue), 8·27; C, 55·14; H, 5·93; N, 7·21. Calc. for $(C_{23}H_{26}O_4N_2H)[Ga(C_{10}H_{12}O_8N_2)(H_2O)]$: Ga, 9·04; C, 51·38; H, 5·36; N, 7·26).

Resolution was attempted by fractional extraction with water.

RESULTS AND DISCUSSION

Fractional crystallization, extraction, and precipitation of the L-strychnine, L-quinine, and D-cinchonine salts of the tris(oxalato)gallate(III) ion effected no alterations in specific rotation from those associated with the initial diastereoisomers. Furthermore, in the fractional precipitation of D-tris(ethylenediamine)cobalt(III) tris(oxalato)-gallate(III), all fractions containing unprecipitated gallate species were optically inactive. These data suggest either that the correct resolving agent for the tris(oxalato)gallate(III) ion has not been used or that resolution cannot be effected because of lack of sufficient stability of the complex species.

That the complex is extensively dissociated in aqueous solution is shown by the immediate precipitation of calcium oxalate upon addition of calcium ion and by the essentially instantaneous exchange with radio-oxalate ion. In two series of experiments, the net activity of the recovered sample was the same, within normal experimental error, after up to 1200 min of equilibrations as at zero time. Exchange was found to be complete in under 1 min. Such extensive dissociation suggests that maintenance of the asymmetric structure long enough to permit resolution is highly unlikely. That the corresponding germanium(IV) species can be resolved[2] is probably due to enhanced stability imparted by the higher cation charge.[13]

Fractional extraction of the L-brucine salt of ethylenediaminetetra-acetatogallic(III) acid gave no indication of resolution of this gallium species. More data based upon salts containing other optically active cations are essential before absolute conclusions on the resolvability of this gallate anion can be reached. In view of the recorded stability of this anion,[7] it is reasonable to assume that successful resolution is as likely with this species as with any gallium(III) chelate.

[13] H. TAUBE *Chem. Rev.* **50**, 69 (1952).

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J. Inorg. Nucl. Chem., 1957, Vol. 5, pp. 57 to 70. Pergamon Press Ltd., London

THE HYDROGEN FLUORIDE SOLVENT SYSTEM—I

A QUALITATIVE SURVEY OF ACIDS*†

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Abstract—In accord with the idea that, as in water and ammonia, acid-base reactions should be possible in hydrogen fluoride and since only substances basic with respect to this solvent were known, a search was undertaken for acids belonging to the hydrogen fluoride system. It was found, as expected, that due to the extremely acid nature of the solvent, the substances capable of acting as acids in it were indeed limited in number. Of all the acids investigated (covering a large portion of the possibilities) the hydrogen fluoride solutions of only four—SbF_5, AsF_5, BF_3, and SnF_4—were found to be capable of dissolving electropositive metals. Many evidences, such as salt formation, were found for the existence of weaker acids. Thus argentous salts were prepared from solutions in HF of BF_3, SiF_4, GeF_4, SnF_4, TiF_4, SeF_4, PF_5, AsF_5, SbF_5, IF_5, VF_5, NbF_5, TaF_5, TeF_6, MoF_6, WF_6, and probably ReF_6. A typical example is the salt $AgAsF_6$. Many of these salts were insoluble in hydrogen fluoride. The phenomenon of amphoterism was demonstrated for salts of trivalent chromium, trivalent antimony, aluminium, and beryllium. Zinc, tripositive iron, and tripositive cobalt were found to be non-amphoteric.

The restrictive effect of co-ordination number was found to be a much severer limitation on the acidity of the fluoroacids than in the case of oxyacids, due to the larger number of fluorine atoms required to form the negative ions. This can easily be seen by comparing PO_4^{-3} and PF_6^-.

IN accordance with solvent theory, any substance increasing the concentration of the anion characteristic of a self-ionizing solvent is a base with respect to that solvent, whereas any substance increasing the cation concentration is an acid.

For the solvents water and ammonia, substances of both kinds are well known. In the case of the only other important binary, protonated, self-ionizing solvent, hydrogen fluoride, however, the existence of only basic substances is usually recognized. If HF be considered to ionize according to the equation

$$2HF \rightleftarrows H_2F^+ + F^-,$$

then any soluble ionic fluoride, such as NaF, will constitute a base.[1] To date, however, with the possible exception of perchloric acid,[2] no substances capable of increasing the "fluoronium" ion (H_2F^+) concentration in hydrogen fluoride have been reported. Indeed, somewhat weaker acids such as nitric have been shown to be definitely basic to hydrogen fluoride.[3]

$$HONO_2 + HF \rightarrow (HO)_2NO^+ + F^-\S.$$

* In part from a dissertation presented by A. F. CLIFFORD to the faculty of the University of Delaware in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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§ The question of whether this would better be written as

$$HNO_3 + 2HF \rightarrow NO_2^+ + H_3O^+ + 2F^-$$

will be the subject of a future paper.

[1] FINBAK *Avh. norske Vidensk. Akad.* No. 6. (1944).

[2] H. FREDENHAGEN *Z. anorg. Chem.* **242**, 23 (1939).

[3] K. FREDENHAGEN *Z. Elektrochem.* **37**, 684 (1931); K. FREDENHAGEN and G. CADENBACH *Z. phys. Chem.* A **146**, 245 (1930).

Even sulphuric acid acts as a base, due to the solvolysis reaction

$$(HO)_2SO_2 + 2HF \rightarrow HOSO_2F + H_3O^+ + F^-.$$

However, in view of the fact that most derivatives of ammonia are basic to water,

$$HNC(NH_2)_2 + H_2O \rightarrow C(NH_2)_3^+ + OH^-,$$

it might be expected by analogy that derivatives of water would in general be basic to hydrogen fluoride. Consequently, acids for the hydrogen fluoride system must be sought among the derivatives of hydrogen fluoride itself.

There are several limitations placed on acids in the hydrogen fluoride system that seldom operate in the water and ammonia systems. Two of these are the limitation of bonding orbitals and the limitation of co-ordination number. The first of these is effective in the fluorides of the second period, CF_4, NF_3, OF_2, where no orbitals are available for such a reaction as

$$2HF + CF_4 \rightarrow H_2F^+ + CF_5^-.$$

Carbon tetrafluoride for example, is not known to form addition compounds of any sort. The reported existence of the substance NF_5[4] has not been confirmed and the existence of the compounds Na_3NF_6 and $NaNF_6$ reported by BECK[5] has been denied.[6] The compounds HNF_2, H_2NF, and HOF would be expected to be basic, comparable to hydroxylamine in water.

The second limitation is exemplified by sulphur hexafluoride, SF_6, where spatial limitations prevent any such reaction as

$$2HF + SF_6 \rightarrow H_2F^+ + SF_7^-,$$

although bonding orbitals are presumably available. Consequently, no fluoroacids comparable to carbonic, nitric, nitrous, or sulphuric acids can be expected to be found. Moreover, the steric factor may be expected to be important in determining the relative strengths of such acids as do exist, as will be seen later.

It was felt that an estimate of the expected degree of acidity for fluorides of about the same degree of ionic nature might be made by comparing boiling-points or Trouton's constants, where available, on the theory that a low degree of association is due to a low degree of ability to share fluorine atoms between molecules and, therefore, would indicate a low degree of ability to remove fluoride ions from hydrogen fluoride and thus a low degree of acidity. By comparing the boiling-points of PF_5, AsF_5, and SbF_5, it should be concluded from this argument that antimony, with a *normal* (i.e. predicted) co-ordination number of 6 toward fluorine (radius ratio[7] = 0·46), would form a much stronger acid than phosphorus and arsenic with normal co-ordination numbers of 4 (radius ratios = 0·25 and 0·35). The same should be true in the series SiF_4, GeF_4, SnF_4. Since tin has a normal co-ordination number of

[4] L. STAUB Dissertation, Breslau, in R. SAMUEL *J. Chem. Phys.* **12**, 180 (1944).
[5] G. BECK *Z. anorg. Chem.* **235**, 45 (1938).
[6] E. ZINTL and W. HAUCKE *Z. anorg. Chem.* **237**, 45 (1938).
[7] L. PAULING *The Nature of the Chemical Bond* Cornell University Press, New York (1945).

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6 (radius ratio = 0·52 with Si = 0·30 and Ge = 0·39) allowing polydimensional association, however, the extreme rise in boiling-point from Ge to Sn must not be considered to indicate an extremely strong acid. In each case, since the intermediate member is on the borderline between co-ordination numbers of 4 and 6, the fluoride should be expected to be of intermediate acidity. All of these predictions will be shown to be true.

In the sulphur family, where the normal co-ordination number never exceeds the oxidation number, the relative boiling-points indicate no good acids. On the other hand, in the boron family, where the co-ordination number always exceeds the oxidation number, the acidity relationships should be expected to parallel those of the water-system acids. Both these sets of relationships were observed.

EXPERIMENTAL

Apparatus

The apparatus used for most of the experimental work was the cylindrical copper vessel shown in Fig. 1. The original liquid delivery lines (one of which is shown) were of copper, but were later replaced with Teflon to avoid contamination of the liquid hydrogen fluoride and chlorine trifluoride delivered through them. The hydrogen fluoride (MATHESON, 99·0 per cent) was taken from the tank, condensed in dry ice, dropped into a trap, revaporized for added purification, and recondensed for delivery to the reactor. The loose-fitting cap was equipped with a Teflon-tipped gas-delivery line used for boron fluoride, fluorine, or other gaseous reagents.

Reactions were carried out in a 50 ml platinum crucible placed under the delivery lines and around which was packed dry ice. The dry ice performed the twofold function of keeping the reactions cold and thereby the hydrogen fluoride liquid, and of preventing influx of atmospheric moisture by its evaporation and consequent outflow. It should be noted that by virtue of the presence of the loose cap and the rapid evolution of CO_2 there was a slight positive pressure inside the reaction vessel. Carbon dioxide neither dissolves in hydrogen fluoride [2] nor reacts with fluorine at room temperature.[8] The reactor itself was also set in dry ice to increase the life of the dry ice inside.

Some preparations and reactions were also carried out in the brass-based, platinum-lined still shown in Fig. 2 (J. Bishop and Company). This still was equipped with both reflux and distillation heads ground to give a tight fit with the still-pot. The reflux head was also equipped with a gas-delivery tube which could be sealed with a ground platinum plug. The pot capacity was 50 ml. All internal joints of the platinum lining were welded, so that the reaction mixture came in contact only with platinum.

Some of the products of reaction described in the following paragraphs were prepared separately in an apparatus in which the HF solvent could be removed under anhydrous conditions. This phase of the work is described in the following paper.

Procedure

Higher fluorides of as many elements as possible were investigated for relative acidity and specificity of reaction. The method of determining relative acidity was in part that of determining the ability of the acids to dissolve metallic fluorides of

[8] H. MOISSAN *Le fluor et ses composés* p. 136. Paris (1900). Revised by MELLOR *Treatise on Inorganic Chemistry* Longmans and Company, Vol. II. p. 12. London (1922).

varying basicity, such as (in order of expected increasing basicity), (CoF_3, MnF_3, CrF_3), HgF_2, AgF_2, CuF_2, (NiF_2, CoF_2), CaF_2, AgF, and NaF, where the compounds within the parentheses are of roughly the same degree of basicity. The solubility of the acid in hydrogen fluoride was considered in the same light, since low solubility would indicate low relative affinity for fluoride ion.

In addition, the ability to dissolve metals was considered to be an important criterion of strength. The metals generally used, roughly in order of increasing electropositivity, were Hg, Ag, Cu, Pb, Sn, Nb, Cr, Zn, Mn, Mg, and Ca.

This criterion depends upon the fact that in order for the metal to dissolve, its protective fluoride coating must be made soluble by reducing the free F^- concentration in solution below that required by the solubility product relationship of the fluoride in question,

$$[M^{+n}][F^-]^n = K_{sp}.$$

Furthermore, since the fluorides of all the metals in this list except Ag are insoluble in pure HF, it follows that for these metals the F^- concentration must be reduced below that existing in HF itself. Consequently, when a substance like SbF_5 brings about dissolution of a metal like Mg or an insoluble fluoride like CeF_3, it follows that the SbF_5 must have acted as an acid, increasing the H_2F^+ concentration of the solution, since, after all, the relationship $[H_2F^+][F^-] = K[HF]$ must be obeyed. (It should be noted that the mere formation of $OH_3^+SbF_6^-$, in case water is present, could not *per se* reduce the F^- concentration below that in pure HF and could therefore not accomplish dissolution of insoluble fluorides.)

Two important reasons for the possible failure of the last criterion are the formation of insoluble films and the slow rate of evolution of hydrogen due to the overpotential of hydrogen on the metal surface. An attempt was made to obviate the first of these by using several different metals whose salts might be expected to vary in solubility. In regard to the second of these, it has been shown[9] that the hydrogen overpotential in HF is much lower than in water. For example, thallium metal, whose normal electrode potential in water is +0·41 V for the reaction $Tl \rightarrow Tl^+ + e^-$, and consequently does not liberate hydrogen from water because of the high hydrogen overpotential, nevertheless was found to dissolve rapidly in liquid HF with liberation of hydrogen. CLIFFORD and BALOG also showed that the hydrogen overvoltage on a dropping mercury electrode was only about 0·4 V in HF compared with around 2 V in water. Thus, the effect of the overpotential factor should be unimportant in liquid HF solutions.

1. *The acids of the nitrogen family.* Antimony pentafluoride, which is liquid between 5 and 150°C, dissolved in hydrogen fluoride with considerable evolution of heat to produce a solution of acidic properties. From this solution a white solid froze out at dry-ice temperature. It was not determined whether this was the simple fluoride or a solvate. The mixed ignited oxides of the lanthanide elements reacted slowly and incompletely and the simple trifluorides reacted rapidly to give clear solutions whose colour depended on which rare-earth metal was dominant and corresponded closely to that of aqueous solutions of the same element. The reaction involved in the case of the fluorides may be formulated as a simple neutralization.

$$NdF_3(c) + 3SbF_5 \rightarrow Nd^{+3} + 3SbF_6^-$$

or

$$NdF_3(c) + 3H_2F^+ \rightarrow Nd^{+3} + 6HF.$$

[9] A. F. CLIFFORD and G. BALOG *Nuclear Sci. Abstr.* **5**, No. 17, 694 (1951).

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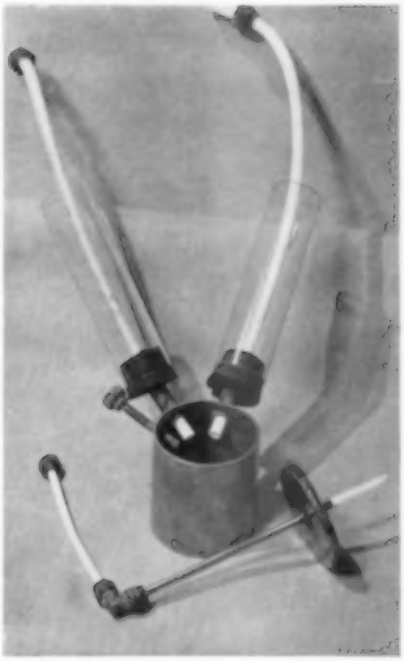

FIG. 1.—Reactor.

FIG. 2.—Platinum still.

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Since in the mixed oxides cerium was present in the tetrapositive state and was taken entirely into solution, the tetravalent rare-earth fluoroantimonates must likewise be soluble. The reaction may be formulated:

$$CeO_2 + 6SbF_5 + 6HF \rightarrow Ce^{+4} + 2H_3O^+ + 6SbF_6^-.$$

On the other hand, it was found that PrO_2 gave Pr^{+3} under these conditions. Sodium fluoride precipitated both oxidation states of rare earths from these solutions, as would be expected of a strong base.

$$3NaF + Nd(SbF_6)_3 \rightarrow NdF_3 \downarrow + 3NaSbF_6.$$

Fluoroantimonic acid solutions reacted with copper metal in the presence of a little moisture to give a bright yellow, apparently colloidal solution ($Cu(SbF_6)_2$?), from which either sodium fluoride or additional fluoroantimonic acid precipitated all the colour as a yellow solid.

Silver fluoride reacted to give a white insoluble salt, presumably $AgSbF_6$.

Sodium fluoride in moderate concentration precipitated the sparingly soluble sodium salt. It is interesting to note the parallelism between the low solubility of $NaSbF_6$ in hydrogen fluoride and the low solubility of $NaSb(OH)_6$ in water.

Cobalt trifluoride dissolved in concentrated fluoroantimonic acid to give a bright cherry-red solution. On dilution with hydrogen fluoride, however, the salt suffered solvolysis, the cobalt trifluoride precipitating out. Since analysis of the precipitate showed no antimony to be present, it was not a basic salt, such as CoF_2SbF_6. The precipitate on treatment with aqueous hydrochloric acid generated chlorine, showing the cobalt to be still trivalent.

Fluoroarsenic acid was prepared by the action of chlorine trifluoride (HARSHAW) on a suspension of arsenic metal in hydrogen fluoride. The reaction proceeded with considerable vigour, dense white fumes, presumably AsF_5, being given off, if the reaction were allowed to run too fast. The solution did not dissolve CoF_2 or CuF_2, but produced a white precipitate with silver fluoride, presumably $AgAsF_6$.

Fluoroarsenic acid did not attack metallic copper or beryllium. It vigorously attacked metallic magnesium (which is not attacked by chlorine trifluoride in hydrogen fluoride), manganese, chromium, niobium, silver, mercury, and lead (the last slowly) with evolution of gas. (It was not determined whether solution was accomplished by liberation of hydrogen or by reduction of the pentavalent arsenic. Perhaps, as with aqueous nitric acid, both mechanisms were operative, the predominance of one over the other depending on concentration and the oxidation potential of the metal being dissolved.) Presumably the niobium dissolved to give fluoroniobic acid, as will be seen later. The fluoroarsenates of magnesium, manganese (deep pink in solution) and chromium were moderately soluble. The fluoroarsenates of silver, lead, and mercury were white and insoluble.

Fluorophosphoric acid was prepared by the fluorination with chlorine trifluoride of a suspension of red phosphorus. (During early runs, a white suspension persisted throughout this (vigorous) reaction. This was attributed to contamination by copper, and, therefore, may have been a fluorophosphate of copper. The suspension was no longer observed after the copper lines were replaced with Teflon.)

Fluorophosphoric acid was classified as a weak acid from its apparent inability to react with Hg_2F_2, HgF_2, CoF_2, CoF_3, and MnF_3. Argentous fluoride

dissolved in fluorophosphoric acid to give a colourless solution which deposited a white salt on evaporation subsequently shown to be $AgPF_6$. (Argentous fluoride alone gives a colourless solution in hydrogen fluoride, but is deposited as a tan solid on evaporation of the solvent.) When fluorophosphoric acid contacted silver difluoride, there appeared to be produced a trace of insoluble blue reminiscent of argentic fluoroborate described below.

Fluorophosphoric acid apparently did not react with metallic calcium, magnesium, manganese, zinc, chromium, and tin, thus definitely having less solvent power than fluoroarsenic acid. Silver dissolved with effervescence, leaving on evaporation a white salt, or in larger amount producing immediately a white precipitate. The fact that tin did not react with another portion of this same solution and that there was some residual phosphorus from the original fluorination still present eliminates the possibility of the presence of chlorine trifluoride during this reaction.

The fluorophosphoric acid after hydrolysis did not decolourize permanganate, showing the phosphorus to be entirely pentavalent.

Fluorobismuthic acid was not investigated.

2. *Boron fluoride*. Rare-earth fluoroborates were prepared by suspending the simple fluorides in ethereal boron fluoride (EASTMAN). An exothermic reaction ensued and solid fluoroborates of very light but characteristic colour were produced. The excess boron fluoride was washed out with ether. Although these salts deliquesced rapidly in air, they were insoluble in hydrogen fluoride. That this insolubility was not a result of the method of preparation is shown by the fact that similar precipitates could be obtained by leading boron fluoride (MATHESON) into rare-earth fluoroantimonate solutions and that boron fluoride did not cause dissolution of rare-earth fluorides in hydrogen fluoride. Fluoroboric acid reacted only very slowly and incompletely with mixed ignited rare-earth oxides.

Attempts to precipitate a pentavalent salt, $Ta(BF_4)_5$, with boron fluoride from a solution of K_2TaF_7 (Fisher Scientific Company) were unsuccessful. Probably, therefore, TaF_5 is too acidic to produce a cation in hydrogen fluoride.

Argentous fluoride precipitated a white, insoluble salt from fluoroboric acid solutions. Subsequent studies on this reaction have shown the precipitate to be $AgBF_4$. Cobaltous fluoride dissolved to some extent. Copper metal reacted as with fluoroantimonic acid in the presence of atmospheric oxygen to produce a yellow compound of low solubility. Solutions of $Cu(H_2O)_x^{+2}$, prepared by saturating 48 per cent aqueous HF (BAKER and ADAMSON) with CuF_2 and diluting 100-fold with anhydrous HF, also gave a yellow precipitate on addition of BF_3 or $NaBF_4$. Argentic fluoride, AgF_2, appeared to be metathesized by fluoroboric acid to a prussian-blue insoluble compound. Cobalt trifluoride, however, did not appear to react.

Magnesium and manganese metals reacted vigorously with fluoroboric acid to give clear solutions, colourless and light pink respectively. When the reaction subsided it was renewed by additional boron fluoride. Addition of sodium fluoride immediately quenched the reaction, showing it definitely to be an effect of acidity. Chromium metal reacted very slowly to give a flocculent green precipitate and a green solution. The low solubility of chromic fluoroborate suggests that the inability of fluoroboric acid to dissolve cobalt trifluoride may have been due, at least in part, to the insolubility of the cobaltic salt, although some colour change might have been expected if an insoluble salt had been formed.

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Metallic beryllium, aluminium, niobium, tin, lead, mercury, and silver appeared not to react with fluoroboric acid.

Sodium and potassium fluoroborates were found to be soluble in hydrogen fluoride, the latter salt giving an approximately 1-molar solution at saturation at 0°C.

It would appear from this evidence that fluoroboric acid is a weak acid in hydrogen fluoride of the same order of strength as fluorantimonic acid, or possibly slightly stronger.

3. *Oxygen family acids.* For the reasons already discussed, sulphur hexafluoride was not investigated.

The fluorination of powered selenium, as described for phosphorus and arsenic, proceeded smoothly and rapidly. The valence of the fluorinated selenium was determined to be 4 by the fact that the solution after hydrolysis and evaporation of hydrogen fluoride was found to be reduced quickly to red elemental selenium on warming with dilute sulphuric acid and sodium bisulphite. Treatment with hot concentrated hydrochloric acid and then more bisulphite produced very little more red selenium. This series of reactions distinguishes between tetra- and hexapositive selenium.[10]

Silver difluoride did not react with fluoroselenious acid. Silver monofluoride failed to produce a precipitate until the silver concentration was fairly high. That this may be due to the weakness of the acid rather than the high solubility of the salt is strongly indicated by the extensive solvolysis, as discussed in the following paper.

Calcium, magnesium, manganese, zinc, chromium, lead, copper, and silver metals were not attacked by fluoroselenious acid.

Tellurium was fluorinated in like manner. The fact that the slightly ammoniacal hydrolysed solution oxidized potassium iodide to free iodine was taken as proof of the hexavalency of the tellurium. (Tetravalent tellurium forms TeI_6^{-2}.) Excess tellurium ensured the absence of chlorine trifluoride. The acid failed to react with CuF_2, AgF_2, HgF_2, CoF_2, CoF_3, and MnF_3. Its argentous salt, which has been shown to be $AgTeF_7$ (see the following paper), was moderately soluble. The acid did not react with metallic magnesium, manganese, or chromium, but produced a black coating on tin. Silver metal reacted to produce a white precipitate.

4. *The halogen acids.* A solution of sodium fluoride in hydrogen fluoride to which chlorine trifluoride was added retained none of the chlorine trifluoride on evaporation of the solvent. Chlorine trifluoride solutions showed little or no solvent power for insoluble metallic fluorides or electropositive metals. Thus, chlorine trifluoride would appear to have the least possible acidic properties. However, pure liquid chlorine trifluoride did dissolve antimony trifluoride on refluxing to give a clear, essentially colourless solution. Surprisingly, it was found that on evaporation the solid residue contained antimony for the most part still in the trivalent state, though there was some evidence of partial oxidation.

Iodine was fluorinated as described for arsenic, etc. The reaction proceeded smoothly with formation of a white solid which, however, dissolved on warming the mixture to room temperature. The valence state of the iodine was determined by treating the hydrolysed and evaporated solution with excess boric acid and testing for periodate by warming with manganous sulphate. The non-oxidation of the manganous ion to permanganate showed the absence of periodate. Therefore, since

[10] E. MÜLLER *Z. phys. Chem.* **100**, 346 (1922).

apparently no lower fluorides of iodine than the pentafluoride can exist,[11] the iodine must have been pentavalent. In further proof of the valence of the iodine, a sample of known iodine pentafluoride was shown to react identically to the fluorinated iodine described.

Fluoroiodic acid did not react with AgF_2, CuF_2, HgF_2, CoF_2, CoF_3, MnF_3, or the metals magnesium, manganese, tin, and copper. Argentous fluoride in excess precipitated the sparingly soluble white argentous fluoroiodate. Silver metal was attacked, developing a white coating, and mercury reacted vigorously, producing a white insoluble compound, which may have been either the fluoroiodate or only mercuric fluoride.

From these data it would appear that the acidity of most of the halogen fluorides is of a low order.

5. *Carbon family acids.* Of this family it was already known that CF_4 has no acid properties and that those of SiF_4 are too feeble for even alkali fluorosilicates to exist in hydrogen fluoride solution.[3]

Although fluorosilicic acid is so extremely weak relative to hydrogen fluoride, it was decided to see whether an insoluble silver salt like those of fluorogermanic and fluorostannic acids (described below) could be prepared.

Fluorination of silicon metal by chlorine trifluoride with subsequent addition of silver fluoride produced no precipitate. However, when the fluorination was carried out in the presence of silver fluoride, a white insoluble compound, presumably Ag_2SiF_6 or more probably $AgSiF_5$, was formed. Thus the solubility of silicon fluoride and and also its acidity in hydrogen fluoride must be very low.

The fluorination of germanium metal with chlorine trifluoride proceeded easily. When the reaction mixture was kept at dry-ice temperature and if the concentration of germanium were high, a white precipitate was obtained. When the temperature was raised, well below the boiling-point of the hydrogen fluoride the solid disappeared and copious white fumes were evolved. (The sublimation point of GeF_4 is $-37°C$.)

Fluorogermanic acid solutions showed no tendency to react with cobalt difluoride or metallic magnesium, manganese, or silver. Argentous fluoride, however, precipitated a white salt from the solution. The low but definite solubility of germanium fluoride places it, as expected, between the tetrafluorides of silicon and tin in acidity.

Tin fluorinated easily with chlorine trifluoride to the stannic state. The acid was very soluble in hydrogen fluoride, the solution evaporating to a point of high viscosity before solidifying. (Stannous fluoride was found to be only very slightly soluble in HF.) The acid did not react with AgF_2, HgF_2, CrF_3, or CoF_3, but gave a white insoluble salt with AgF. Calcium, beryllium, and manganese metals were apparently not attacked by it. Magnesium reacted very slowly.

6. *Acids of the transition elements.* The elements chromium and manganese in their higher valence states, because of the restriction of co-ordination number, appeared not to be suitable candidates for fluoroacids and were, therefore, not investigated, although CrF_5 might well be acidic in HF. Metallic titanium, vanadium, niobium, molybdenum, tungsten, and rhenium, however, were fluorinated as described for phosphorus.

[11] O. RUFF and A. BRAIDA *Z. anorg. Chem.* **220**, 43 (1934).

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Titanium tetrafluoride so produced was only sparingly soluble in hydrogen fluoride, precipitating as a white solid. That it did have some feebly acidic properties, however, was shown by its dissolution on addition of sodium fluoride. Apparently, also, titanium fluoride underwent reaction with cupric fluoride to produce a blue, slightly soluble salt closely resembling cupric fluoride itself, but, unlike cupric fluoride, insoluble also in 48 per cent aqueous hydrofluoric acid. The supernatant solution over the titanium fluoride did not react with metallic silver or mercury, but did produce a white precipitate with argentous fluoride.

Vanadium metal fluorinated with difficulty because of the formation of a protective coating of the green lower fluoride, VF_3. A yellow supernatant liquid was obtained, presumably containing some VF_5. The fluorovanadic acid solution appeared to be able to dissolve cupric and praseodymium fluorides, but not cobaltic fluoride. Argentous fluoride dissolved without forming a precipitate; therefore, argentous fluorovanadate must be fairly soluble.

The fluorination of niobium metal was extremely vigorous and was accompanied by brilliant scintillation. A colourless solution was obtained which evaporated only slowly at room temperature, but eventually deposited white niobium pentafluoride. Fluoroniobic acid did not react with AgF_2, HgF_2, CoF_2, NiF_2, or MnF_3. It gave with AgF a colourless salt of limited solubility which could easily be made to precipitate with an excess of silver fluoride. The acid very slowly developed a brown coating on silver metal, but did not react with magnesium.

Free fluorotantalic acid was not prepared. Potassium fluorotantalate, K_2TaF_7 (FISHER), however, was found to be quite soluble. From a solution of this salt, white insoluble argentous fluorotantalate was precipitated by AgF. Fluorotantalic acid is probably comparable in acidity to fluoroniobic.

Metallic molybdenum fluorinated to a colourless solution, which at high concentration precipitated a white solid. Since this solid melted at room temperature and vaporized, it was without question MoF_6. The precipitated MoF_6 dissolved on addition of NaF. The fluoromolybdic acid solution reacted with cupric fluoride to give a bright yellow compound which returned to the blue of hydrated cupric fluoride on evaporation in air. Argentous fluoride in excess precipitated a white compound. The acid did not attack magnesium or manganese metals. Silver dissolved with some effervescence and formation of a brownish coating on the surface of the metal.

Tungsten fluorinated with less vigour giving a soluble product. The bases CoF_2 and CoF_3 did not react with the acid. Cupric fluoride dissolved to some extent, giving a greenish yellow solution and suspension from which metallic tin reduced out copper metal. As with cupric fluoromolybdate, however, on evaporation in air the colour of the residue was that of hydrated CuF_2. Argentous fluoride dissolved, but deposited a white salt on evaporation, whereas AgF itself would have been tan. The acid did not react with magnesium or zinc. Silver, however, dissolved with evolution of gas. Although the reactions of MoF_6 and WF_6 with Ag metal might possibly be due to the presence of residual ClF_3, the dissolution of the solids in NaF solution and the precipitation of the white silver salts (both reactions in basic solution) cannot. These "acids" probably hardly disturb the $2HF \rightleftarrows H_2F^+ + F^-$ equilibrium.

It may be pointed out that Mo and W easily increase their co-ordination number toward small groups to greater than 6, e.g. $K_3W(CN)_8$, $K_3Mo(CN)_8$, $(NH_4)_3$-MoO_2F_5.

Attempts to fluorinate rhenium in the usual way met with poor success because of the formation of a protective coating of the green lower fluoride ReF_4. Accordingly, the metal was refluxed for 5 hours in a mixture of hydrogen fluoride and chlorine trifluoride. The reaction again was incomplete. The resulting solution was a deep dirty yellow, presumably containing ReF_6 and ReF_4 in solution or suspension. It reacted with AgF to precipitate an insoluble salt, white to peach in colour, which may have been the salt of either valence state. Calcium fluoride dissolved to some extent, giving a greenish solution, the colour undoubtedly indicating the presence of tetravalent rhenium. Cobaltous fluoride did not react. Metallic tin reacted first vigorously, then more slowly to give a black coating of rhenium metal on its surface. Magnesium and manganese did not react.

7. *Ampholytes.* The phenomenon of amphoterism should be expected to have the same manifestations in hydrogen fluoride as in other self-ionizing solvents. Thus it was found that cryolite, Na_3AlF_6, was quite soluble in hydrogen fluoride, but precipitated white aluminium fluoride on treatment with boron fluoride. Likewise, potassium fluorochromite, K_3CrF_6, was soluble in hydrogen fluoride, but, like its hydroxy analogue, was easily solvolysed, precipitating green chromic fluoride. This precipitate was dissolved by excess sodium fluoride. This solution treated with excess boron fluoride gave a green precipitate, with green also left in solution. Ammonium fluoroberyllate, $(NH_4)_2BeF_4$, was quite similar to sodium fluoroaluminate in its reactions.

Antimony trifluoride, itself insoluble in HF, dissolved in a large excess of NaF. However, although PbF_2 and SnF_2 showed very slight solubility in very concentrated NaF solutions, ZnF_2, FeF_3 and CoF_3 showed no detectible solubility. These reactions clearly show the amphoteric characteristics of aluminium, beryllium, tripositive chromium, and tripositive antimony and the non-amphoteric nature of zinc, tripositive iron, and tripositive cobalt.

DISCUSSION

Synopses of the qualitative solubilities in hydrogen fluoride of the salts of the fluoroacids that were observed with reasonable certainty and of the reactions of the fluoroacids with metals are shown in Tables 1 and 2. On the basis of these data the fluorides have been classified according to acid strength by means of the following categories (shown in Table 3). (1) dissolve CoF_3, (2) dissolve Cr, Mn, (3) dissolve Mg or react with CoF_2, CuF_2, AgF_2, (4) form salt with AgF, (5) very weak (solution unstable), (6) amphoteric, (7) neutral, (8) soluble strong bases, including the fluorides of the alkali metals, Ra, Ba, Sr, Ca, Ag^+, and Tl^+. (Though apparently forming a cupric salt, titanium tetrafluoride was placed in category (6) because of its low solubility.) It must be pointed out in defence of category (5) that in the case of the similar highly polar solvent water, it is invariably true that if a compound is a strong acid of simple molecular structure, it is highly soluble. This is not, of course, true for less polar solvents, as for example liquid ammonia, nor is the converse of the statement true.

Some interesting salt-solubility relationships may be noted—the regular decrease in solubility of the argentous salts of the acids in both fifth-column families as one passes down the columns, the uniform insolubility of the argentous salts of the fourth-column families, the regular decrease in solubility of the fluoroborates as one

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TABLE 1.—SOLUBILITIES OF SALTS OF THE FLUOROACIDS

Acid	Soluble	Sparingly soluble	Insoluble
BeF_2	NH_4^+, Na^+		
BF_3	Na^+, K^+, Mg^{+2}, Mn^{+2}	Co^{+2}, Cr^{+3}	Ag^+, Cu^{+2}, Ag^{+2}, Ce^{+3}, Ce^{+4}
AlF_3	Na^+		
CrF_3	Na^+, K^+ (solvolyse)		
SiF_4	Na^+, K^+ (decompose)		Ag^+
GeF_4	Na^+		Ag^+
SnF_4		Cu^{+2}	Ag^+
TiF_4	Na^+	Cu^{+2}	Ag^+
ReF_4?	Ca^{+2}		Ag^+?
SeF_4	Ag^+, Hg_2^{+2}?		Cu^{+2}, Hg^{+2}
PF_5		Ag^+	Cu^{+2}, Ag^{+2}?
AsF_5	Mg^{+2}, Mn^{+2}, Cr^{+3}		Ag^+, Ag^{+2}, Pb^{+2}, Hg^{+2}
SbF_5	Ce^{+3}, Co^{+3}, Ce^{+4}	Na^+	Ag^+, Cu^{+2}
BiF_5		K^+?	
VF_5	Ag^+, Cu^{+2}?, Pr^{+3}?		Hg^{+2}
NbF_5		Ag^+	
TaF_5	K^+		Ag^+
IF_5		Ag^+	Hg^{+2}
TeF_6		Ag^+	
MoF_6	Na^+	Ag^+, Cu^{+2}	
WF_6	Ag^+	Cu^{+2}	
ReF_6	Ca^{+2}		Ag^+?

TABLE 2.—REACTIONS OF METALS WITH FLUOROACIDS

Acid	Reaction	Slow reaction	No reaction
BF_3	Mg, Mn	Cr	Be, Al, Nb, Sn, Pb, Hg, Ag
GeF_4			Mg, Mn, Ag
SnF_4		Mg	Ca?, Be, Mn
TiF_4			Hg, Ag
SeF_4			Ca, Mg, Mn, Zn, Cr, Pb, Cu, Ag
PF_5	Ag		Ca, Mg, Mn, Zn, Cr, Sn
AsF_5	Mg, Mn, Cr, Nb, Pb, Hg, Ag		Cu, Be
VF_5	Hg, Ag		Mg, Nb
NbF_5		Ag	Mg
IF_5	Hg, Ag		Mg, Mn, Sn, Cu
TeF_6	Sn, Ag		Mg, Mn, Cr
MoF_6		Ag	Mg, Mn
WF_6	Ag		Mg, Zn
ReF_6	Sn		Mg, Mn

TABLE 3.—RELATIVE STRENGTHS OF FLUOROACIDS IN HF

Group	Category			Increasing acidity			
	7	6	5	4	3	2	1
IIA		Be(II)					
IVA			Ti(IV)				
VA				Nb(V) Ta(V)	V(V)		
VIA		Cr(III)			Mo(VI) W(VI)		
VIIA					Re(VI)		
IIIB		Al(III)				B(III)	
IVB	C		Si(IV)	Ge(IV)	Sn(IV)		
VB	N	Sb(III)			P(V)	As(V)	Sb(V)
VIB	O, S(VI)		Se(IV)	Te(VI)			
VIIB	F, Cl(III)			I(V)			

passes from left to right in the Periodic Table (Mg^{+2} to Co^{+2} to Cu^{+2}) or as the valence increases (Mn^{+2} to Cr^{+3} to Ce^{+4}), and the decrease in solubility of the fluoroarsenates as one passes from light to heavy metals (Mg^{+2}, Mn^{+2}, Cr^{+3}, and Ag^{+}, Pb^{+2}, Hg^{+2}).

It can be seen from the breakdown presented in Table 3 that the ability of the various elements to form fluoroanions, as predicted, apparently does not correspond entirely to their ability to form oxy anions, but is more severely restricted by steric factors. These are the same steric factors, indeed, which in the water system, without eliminating the ability to form acids (thanks to the divalency of oxygen), dictate the change in co-ordination number from HNO_3 to H_3PO_4 to H_7SbO_6, from H_2SO_4 to H_6TeO_6, and from $HClO_4$ to H_5IO_6. Thus, in those families in which the oxidation number is sufficiently high (4 or more) so that the stable co-ordination number for fluorine with respect to the central atom may for some members be not greater than the oxidation number, the effect is quite evident. The carbon and nitrogen families are particularly graphic examples of this, the relative acidities being just the opposite of those of the corresponding oxyacids. As would be expected because of the higher valence, however, the acids of the nitrogen family are generally stronger than those of the carbon family. In the oxygen family, the limitation of acidity by preference for a co-ordination number of 6 is quite evident in the decrease in acidity of TeF_6 from that of SbF_5. The same limitation is undoubtedly operative in the halogen, chromium, and manganese families.

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On the other hand, where the valence is such that an adequate co-ordination number for stable anion formation is allowed for all members of a family, it should be expected that, as with oxyacids, the acidity would not increase, but rather would decrease with increasing atomic radius. This is observed in the beryllium and boron families. From the same point of view, it might be predicted that fluoroplumbic and fluorobismuthic acids would be less acidic than fluorostannic and fluoroantimonic. Conversely, since polonium may be able to co-ordinate seven or eight fluorine atoms with greater ease than tellurium, it might be predicted that the fluoropolonate ion might be reasonably stable and that PoF_6, therefore, would be a stronger acid than TeF_6.

The steric effect (normal co-ordination number) may be seen operating in the low acidity of IF_5 compared with that of SbF_5. The configuration of IF_5 has been shown to be that of a square pyramid, which implies an octahedral distribution of five fluorine atoms and one unshared pair of electrons about the central iodine atom—in other words, a co-ordination number of 6. Since 6 is the normal co-ordination number of iodine, there will be far more steric resistance against addition of a fluoride ion to IF_5 (co-ordinatively saturated) than to SbF_5, which is co-ordinatively unsaturated. (In IF_6^- the unshared pair has been repressed by the added F^-). The same situation exists in ClF_3, where the chlorine atom (normal co-ordination number 4) has an actual co-ordination number of 5 (three fluorine atoms and two unshared pairs of electrons). (It should be noted that in the tetrahedral BrF_4^-, the unshared pairs have again been repressed.)

The ability of many of these acids to attack silver and mercury, although only SbF_5, AsF_5 and BF_3 solutions could attack magnesium, with liberation of hydrogen is not inconsistent with the known fluorinating power of the simple fluorides. In those cases where no fluorinating properties are expected, no attack should be observed on silver or mercury. Thus fluoroboric acid which dissolved magnesium did not attack the noble metals. On the other hand, solutions of AsF_5, VF_5, IF_5, TeF_6, MoF_6, WF_6, and ReF_6, which might be expected to have considerable oxidative power, did attack silver and mercury. Their action may be likened to that of aqueous nitric acid on copper. Typical reactions may be

$$3AsF_6^- + 2Ag + 3H_2F^+ \rightarrow 2AgAsF_6 + AsF_3 + 6HF$$

$$6AsF_6^- + 5Ag + 6H_2F^+ \rightarrow 5AgAsF_6 + As + 12HF$$

$$6AsF_6^- + 8Ag + 6H_2F^+ \rightarrow 5AgAsF_6 + Ag_3As + 12HF$$

$$6IF_6^- + 6Ag + 6H_2F^+ \rightarrow 5AgIF_6 + AgI + 12HF$$

$$2TeF_7^- + 3Sn + 8HF \rightarrow 3SnF_6^{-2} + 2Te + 4H_2F^+.$$

Fluoroarsenic acid may react by both mechanisms. The reduction of NbF_5 seems less likely and should be reinvestigated.

The ability of these acids to react with silver and mercury but not with copper and the electropositive metals undoubtedly is related to their weakness as acids. Since the product of the fluorination of silver is the soluble strong base, AgF, the silver goes into solution and subsequently, when the argentous ion concentration is high enough, may precipitate the silver salt of the weak acid with which the silver is reacting. With mercury, the insolubility of mercuric fluoride cannot protect the

metal from attack because of its inability to cling to the liquid surface. In the case of all other metals that form insoluble bases, however, if the acid involved is not strong enough to dissolve the insoluble base formed by the fluorination reaction, as for instance $IF_6^- + 3Mn + H_2F^+ \rightarrow 3MnF_2 + HI \uparrow + HF$, the formation of a very thin film of the base on the metal surface will protect it from further attack.

It follows, then, that in the case of those acids which are neither strong acids nor good oxidants, no reaction at all with metals is to be expected. This was observed with TiF_4, GeF_4, and SeF_4.

Considering the fact that the strongest acid found, SbF_5, forms a cobaltic salt which is completely solvolysed in dilute solution, and that ferric and aluminium acetates are hydrolysed in aqueous solution, we may consider fluoroantimonic acid to be somewhat less strong relative to hydrogen fluoride than acetic acid is relative to water. All the acids of the hydrogen fluoride system which were investigated must, therefore, be of very low strength relative to the solvent; indeed, such that slightly poorer acids than SbF_5 (e.g. PF_5) can no longer dissolve electropositive metals.

Nevertheless, despite the relative weakness of the fluoroacids, acid-base phenomena have been amply demonstrated for the hydrogen fluoride system.

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THE HYDROGEN FLUORIDE SOLVENT SYSTEM—II

SALTS OF THE FLUORO ACIDS. SOLVOLYSIS*

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Abstract—The stoichiometries of a number of solid salts of fluoro acids have been determined by evaporation of anhydrous HF solutions of the salts containing excess of the volatile acidic constituent. Salts of fluoro acids of P, As, Ge, Se, Te, and I have been examined. Many of these are highly solvolysed. The new bifluoride $BaHF_3$ is reported.

THE present study was undertaken in order to provide quantitative information on some of the reactions discussed in the preceding paper (CLIFFORD, BEACHELL, and JACK). Because of the necessity for isolating precipitates quantitatively and since at the time of this work filter materials which could be used in anhydrous HF were not available, it was decided to limit this study entirely to salts of volatile fluoro acids so that the salts could be prepared in the presence of an excess of the acid and the excess acid subsequently removed by evaporation. The weakness of many of the investigated acids relative to HF was apparent from extensive solvolysis and resultant loss of the acidic constituent during evaporation of the solutions.

Apparatus and procedure. The apparatus used for preparation of the acids was similar to that described in the preceding paper. Fluorination was carried out at dry-ice temperature, using a weighed sample of the acid-forming element to be fluorinated and ClF_3 as agent. When reaction was complete, a sample of a "basic" metal fluoride was added from a platinum container, the weight being taken by difference. The platinum crucible was then quickly removed to a polyethylene chamber connected to a drying train. Air was pulled rapidly by means of a water-pump through a rotometer, two sulphuric acid-traps, two glass-wool traps, through a Drierite tower, and thence into the top of the polyethylene drying chamber, which was a bottle cut off at the bottom and set in a mercury pool. Within the chamber the platinum crucible containing the sample sat on a little platform above the mercury surface. From the drying chamber the air, HF, and other volatile substances were drawn through Drierite and concentrated aqueous KOH. The rapid passage of air through the system was adequate to prevent diffusion of water vapour back in, as was shown by the fact that an open weighing bottle containing P_2O_5 gained only 2 mg over an 18 hr period. (This gain may in large part have resulted from the handling necessary for weighing it.) Drying of the sample was continued until it reached constant weight.

EXPERIMENTAL

Phosphorus. A suspension of red phosphorus in HF was fluorinated by dropwise addition of ClF_3. That the product was PF_5 was shown by the lack of reaction of the

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hydrolysed product with acidic potassium permanganate. Reactions were carried out with less than the equivalent amount of AgF, NaF, BaF_2, and CaF_2, and the solutions were then evaporated as described above. The following data are the averages of several runs in each case.

TABLE 1.—FLUOROPHOSPHATES

Base added		Product obtained				
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.	Slbty in HF
AgF	0·5398	1·0777	1·0752	$AgPF_6$	+0·3	sol.
BaF_2	0·4662	1·1088	1·1360	$Ba(PF_6)_2$	−2·4	sol.
NaF	0·3312	1·2977	1·3247	$NaPF_6$	−1·9	sol.

Arsenic. Fluorination was carried out on a suspension of metallic arsenic in the same manner as with phosphorus, yielding AsF_5.

TABLE 2.—FLUOROARSENATES

Base added		Product obtained				
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.	Slbty in HF
BaF_2	0·1999	0·5991	0·5874	$Ba(AsF_6)_2$	+2·0	mod. sol.
NaF	0·1913	0·9941	0·9652	$NaAsF_6$	+3·0	sl. sol.

Antimony. (In a subsequent study[1] the solubility of $NaSbF_6$ in liquid HF at 2°C was determined to be 0·2 molar. Volumetric samples of the saturated solution of pure $NaSbF_6$ were taken and, after evaporation of the HF, analysed for antimony by the method of VORTMANN and MENTZEL.[2])

Boron. (The solubility of KBF_4 in HF at 2°C has been determined[1] to be 0·48 molar. Evaporated volumetric samples of the saturated solutions were analysed for boron and fluorine by the procedure of BOOTH and MARTIN[3] and for potassium by the procedure of SCHWARBOLD and KOHLER, as summarized by GLOSS.[4]) The quantitative precipitation of $AgBF_4$ from HF solutions will be described in the following paper.[5]

Tellurium. Crushed tellurium slab in HF was fluorinated as before. That the product was TeF_6 was shown by the ability of the hydrolysed solution to liberate I_2 from KI. Solid TeF_6 was observed to crystallize out of concentrated solution at −78°C in large, clear crystals.

(1) A. F. CLIFFORD and L. DAUERMAN Unpublished work.
(2) G. VORTMANN and A. MENTZEL *Scott's Standard Methods of Chemical Analysis* (Fifth Edition) Vol. I. p. 72. Van Nostrand, New York (1939).
(3) BOOTH and MARTIN *Boron Trifluoride and its Derivatives* p. 238. J. Wiley, New York (1949).
(4) G. H. GLOSS *Chem. Anal.* **42**, 50 (1953).
(5) A. F. CLIFFORD and S. KONGPRICHA Unpublished work.

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TABLE 3.—FLUOROTELLURATES

Base added		Product obtained				
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.	Slbty in HF
AgF	0·1786	0·5313	0·5187	$AgTeF_7$	+2·4	mod. sol.
BaF_2	0·2532	0·7869	0·6018	$BaTeF_8$	+30·7	sol.
			0·9492	$Ba(TeF_7)_2$	−17·3	
CaF_2	0·1328	0·8010	0·5437	$CaTeF_8$	+47·3	sol.
			0·9544	$Ca(TeF_7)_2$	−16·1	

Selenium. Fluorination of selenium metal was carried out as above, the product, however, being SeF_4, as shown by the ready reduction of the hydrolysed solutions by bisulphite.

TABLE 4.—FLUOROSELENITES

Base added		Product obtained				
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.	Slbty in HF
BaF_2 in 20 ml HF	0·1810	0·2308	0·3437	$BaSeF_6$	−32·9	sol.
			0·2017	$BaHF_3$		
BaF_2 in 30 ml HF	0·1813	0·2174	0·3442	$BaSeF_6$	−36·9	sol.
			0·2020	$BaHF_3$		
NaF	0·1447	0·2423	0·6786	$NaSeF_5$	−64·3	sol.
			0·2136	$NaHF_2$		

Iodine. Fluorination of elemental iodine with ClF_3 in HF proceeded very easily. The absence of IF_7 was shown by the inability of the hydrolysed solutions to oxidize manganous sulphate solutions.

TABLE 5.—FLUOROIODATES

Base added		Product obtained				
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.	Slbty in HF
BaF_2	0·1937	0·3236	0·6832	$Ba(IF_6)_2$	−52·6	sol.
			0·4388	$BaFIF_6$	−26·3	
			0·2158	$BaHF_3$		
NaF	0·1971	0·3150	1·2357	$NaIF_6$	−74·5	mol. sod.
			0·2910	$NaHF_2$		

Germanium. Fluorination of metallic germanium with ClF_3 at −20°C proceeded readily.

TABLE 6.—FLUOROGERMANATES

Base added		Product obtained				
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.	Slbty in HF
BaF_2	0·1658	0·4110	0·4468 0·3064	$Ba(GeF_5)_2$ $BaGeF_6$	− 8·0 +25·5	sol.
NaF	0·2172	0·9248	0·9857	$NaGeF_5$	− 8·3	sol.

The barium salts of TeF_6 and SeF_4 were analysed for Te and Se by reduction to the metal and weighing was such. The analyses, though crude, gave qualitative confirmation of the degree of solvolysis indicated by the ratio of product-to-base (Tables 3 and 4).

TABLE 7.—ANALYSES OF FLUOROSELENITES AND -TELLURATES

Components calculated from Tables 3 and 4		Weight of sample (g)	Wt. of non-metal required (g)	Wt. of non-metal found (g)
$BaSeF_6$	10·8%	0·2211	0·006	0·01
$BaHF_3$	89·2%			
$Ba(TeF_7)_2$	53·3%	0·7869	0·285	0·24
$BaTeF_8$	46·7%			

Bifluorides. Solutions of bases in HF evaporated in the absence of acid, but under the same conditions as above gave the following results. Of these, $BaF_2 \cdot HF$ is not previously reported and $LiHF_2$ has just recently been reported.

TABLE 8.—BIFLUORIDES

Base added		Product obtained			
Compound	Wt. (g)	Wt. (g)	Theoretical for		% Dev.
BaF_2	0·5927	0·6598	0·6605	$BaHF_3$	−0·1
LiF	0·1245	0·2195	0·2204	$LiHF_2$	−0·4
KF	0·2365	0·3171	0·3179	KHF_2	−0·2
NaF	0·1475	0·2175	0·2177	$NaHF_2$	−0·1

The HF content of these bifluorides was checked titrimetrically by reacting the aqueous solution or suspension of the bifluoride with excess $CaCl_2$ and titrating with standard base.

E.g.,

$$NaHF_2 + CaCl_2 \rightarrow CaF_2 + NaCl + HCl$$

$$2BaHF_3 + CaCl_2 \rightarrow CaF_2 + 2BaF_2 + 2HCl$$

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The results were as follows:

TABLE 9.—ANALYSES OF BIFLUORIDES

Bifluoride	Weight	0·1 N NaOH (ml)	Required	% Dev.
$BaHF_3$	0·6598	33·40	33·52	−0·3
$LiHF_2$	0·2195	47·64	47·95	−0·6
KHF_2	0·3171	39·89	40·03	−0·4
$NaHF_2$	0·2175	34·98	35·10	−0·3

DISCUSSION

The apparent lack of solvolysis of the soluble salts of AsF_5 and PF_5 indicates that these (as well as SbF_5 and BF_3) are reasonably strong acids relative to the solvent HF. Of the others, the weight obtained indicated the possible compositions shown in Table 10. For preparations under different conditions of concentration and temperature, the compositions can be expected to vary considerably.

TABLE 10.—PROBABLE COMPOSITIONS OF SALTS

	%		%
$BaIF_7$	59·0	$Ba(TeF_7)_2$	53·3
$BaHF_3$	41·0	$BaTeF_8$	46·7
$NaIF_6$	2·5	$Ca(TeF_7)_2$	62·7
$NaHF_2$	97·5	$CaTeF_8$	37·3
$BaSeF_6$	10·8	$Ba(GeF_5)_2$	74·5
$BaHF_3$	89·2	$BaGeF_8$	25·5
$NaSeF_5$	6·2	$NaGeF_5$	90·8
$NaHF_2$	93·8	$NaHF_2$	9·2

It would appear from these data that the soluble salts of the acids GeF_4, TeF_6, IF_5, and SeF_4 are all more or less solvolysed, the solvolysis increasing in the order named. A series of acid strengths can thus be set up as follows: (BF_3, SbF_5, AsF_5, PF_5) $> GeF_4 > TeF_6 > IF_5 > SeF_4$, which is consistent with the relative strengths indicated in the preceding paper.

It should be noted that by such formulas as $BaTeF_8$ nothing more than empirical composition is implied, although it seems likely that the compound might be described as $(BaF)(TeF_7)$, since it would be most surprising if solvolysis of $Ba(TeF_7)_2$ should give $Ba(TeF_8)$. The same arguments apply to $BaIF_7$, $BaSeF_6$, and $BaGeF_6$.

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THE HYDROGEN FLUORIDE SOLVENT SYSTEM—III
THE PREPARATION OF ANHYDROUS SILVER FLUOROBORATE

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Abstract—Pure $AgBF_4$ has been prepared by precipitation from anhydrous HF solutions of $AgNO_3$ with BF_3.

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BECAUSE of its extreme deliquescence and resistance to dehydration without decomposition, anhydrous $AgBF_4$ has not been obtainable until recently. WILKE-DÖRFURT and BALZ[1,2] reported preparation of the hydrates by dissolution of freshly precipitated Ag_2CO_3 in aqueous HBF_4. However, drying even over P_2O_5 led only to $AgBF_4 \cdot H_2O$. Attempts to drive off the water of crystallization by heating resulted in decomposition.

The first reported successful attempt to prepare anhydrous $AgBF_4$ was that of SHARPE,[3] who treated dry $AgBO_2$ with liquid BrF_3. The white residue of $AgBF_4$, insoluble in BrF_3, obtained upon evaporation of the excess BrF_3, gave only a trace of AgBr (derived from $AgBrF_4$ present as an impurity) upon dissolution in water.

Since qualitative studies[4] had shown that $AgBF_4$ is insoluble in liquid HF, the possibility suggested itself of preparing this compound in easily assembled apparatus and with the somewhat more easily handled HF and common reagents.

Since $AgNO_3$ is quite soluble in HF[5] according to the equation

$$AgNO_3 + 2\,HF \rightarrow Ag^+ + H_2NO_3^+ + 2F^-,$$

it seemed a likely starting material which would have no interfering anions, since NO_3^- would not be present in solution as such. The BF_4^- was provided by bubbling BF_3 into the solution,

$$BF_3 + F^- \rightleftharpoons BF_4^-.$$

EXPERIMENTAL

Apparatus. All parts of the apparatus (Fig. 1) coming in contact with liquid HF were built of polyethylene or "Kel-F" (polytrifluorochloroethylene). The polyethylene parts were welded together with a hot nitrogen gun purchased especially for the purpose. The three vessels shown were 6-oz "Boston round" bottles with

(1) E. WILKE-DÖRFURT *Z. angew. Chem.* **37**, 712 (1924).
(2) E. WILKE-DÖRFURT and G. BALZ *Z. anorg. Chem.* **159**, 197 (1927).
(3) A. G. SHARPE *J. chem. Soc.* 4538 (1952).
(4) A. F. CLIFFORD, H. C. BEACHELL, and W. M. JACK *J. inorg. nucl. Chem.* **5**, 57 (1957).
(5) K. FREDENHAGEN, G. CADENBACH, and W. KLATT *Z. physik. Chem.* A **146**, 245 (1930).

standard polyethylene screw caps, which, when greased with fluorolube, were leak-proof under small pressure differentials. The tubing used was $\frac{1}{4}$ in. polyethylene. The parts of the apparatus were

A Trap,
B Reaction vessel,
C Short outlet,
D Outlet just clearing the magnetic stirrer *L*,

and fitted with a porous Kel-F disc acting as filter.

E, F, G Screw-clamps,
H Gooseneck disposal line,
J Outlet through drying tubes to air,
K Disposal vessel.

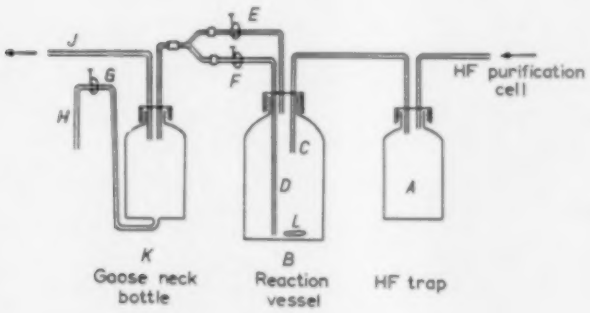

FIG. 1.

Procedure. Silver nitrate, dried at 105°C for 3 hr, was placed in the reaction vessel *B* containing a Teflon-covered magnetic stirring bar *L* and the system was then flushed for 30 min with dry nitrogen. Gaseous HF, purified in the electrolytic cell to be described,[6] was condensed in trap *A* and then redistilled into *B*. The temperature of the reaction vessel was slowly raised to 0°C and the mixture stirred until complete solution of the $AgNO_3$ resulted. With continued stirring and with screw-clamp *F* closed and *E* open, BF_3 was passed in through the HF-inlet trap into the reaction vessel. A white precipitate of $AgBF_4$ formed rapidly. Introduction of BF_3 was continued until no further precipitation was observed. Now by application of a slight pressure of N_2 through the HF-inlet trap, the supernatant solution was forced out through the filter and line *D* into vessel *K*. The precipitated $AgBF_4$ was washed four times with fresh portions of liquid HF to get rid of nitric acid. The waste liquors were ejected through the gooseneck *H*. The system was then flushed for 12 hr with dry nitrogen and then the product was placed in a high vacuum for 12 hr to remove the last traces of HF. It was stored in a polyethylene bottle over P_2O_5. The product was beautiful white, extremely deliquescent crystals, obtained in 85 per cent yield.

Analytical. The brown-ring test with $FeSO_4$ and H_2SO_4 revealed the presence of

[6] A. F. CLIFFORD and J. SARGENT *J. Amer. chem. Soc.* In press. Part IV of this series.

no nitrate. Silver was titrated with standard chloride solution, the endpoint being determined potentiometrically*. Found: 54·32 ± 0·04 per cent. Theoretical: 55·41. Fluoroborate was precipitated as the nitron salt from 5 per cent acetic acid solution after precipitating the silver with an equivalent amount of HCl. This precipitation was done at 0°C and was allowed to stand for 3 hr before filtering. It was dried at 105°C to constant weight. The BF_4^- found was 44·31 ± 1·15 per cent, theoretical: 44·59 per cent.

* The silver analyses were performed by Mr. D. E. HARDIES of this laboratory.

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THE REDUCTION OF PLUTONIUM BY TETRAVALENT URANIUM

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Abstract—The conditions for using U(IV) as a reducing agent for plutonium in HNO_3 and other solutions have been investigated. It is shown that U(IV) quantitatively reduces plutonium to Pu(III) within 5 min in 1 M HNO_3. This fact has been used in liquid-liquid extractions for separating plutonium from uranium, thus giving an aqueous solution of only plutonium, while all of the uranium stays in the organic solvent. The efficiency of aqueous U(IV) solutions to reduce Pu(IV), originally bound as a TTA complex in benzene, has also been studied. The experiments have been performed with tracer concentrations of plutonium at room temperature.

ONE of the main chemical steps in the production of plutonium is the separation of plutonium from uranium. This process is facilitated by the reduction of the former to the trivalent state. Though a considerable number of reducing agents for plutonium have been investigated,[1–4] the use of tetravalent uranium does not seem to have been described previously.

From the standard oxidation-reduction potentials for the various valency states of uranium and plutonium,[5] it can be calculated that the reactions

$$U^{4+} + 2Pu^{4+} + 2H_2O \rightarrow UO_2^{2+} + 2Pu^{3+} + 4H^+ \quad (1)$$

and

$$3U^{4+} + 2PuO_2^{2+} + 2H_2O \rightarrow 3UO_2^{2+} + 2Pu^{3+} + 4H^+ \quad (2)$$

are highly favoured in acid solutions. Thus U(IV) should rapidly reduce the higher valency states of plutonium to Pu(III), provided the activation energy of the reactions is not exceptionally high.

This paper will describe some experiments done to establish the possibilities of using U(IV) as a reducing agent for plutonium, particularly in liquid-liquid extractions and in the presence of HNO_3.

EXPERIMENTAL

Reagents

Uranyl nitrate and perchlorate were obtained by dissolving UO_3 of high purity (obtained from A. B. Atomenergi, Stockholm) in the corresponding p.a. acids. $U(ClO_4)_4$ solutions were prepared by electrolysing $UO_2(ClO_4)_2$ solutions as described elsewhere.[6]

[1] R. E. CONNICK *The Actinide Elements* Chap 8. N.N.E.S. Vol IV-14a. McGraw-Hill, New York (1954).
[2] B. GOLDSCHMIDT, P. REGNAULT, and I. PREVAT *Proc. Geneva Conf.* Paper P/349 (1955).*
[3] E. K. HYDE *The Actinide Elements* Chap. 15. N.N.E.S. Vol IV-14a. McGraw-Hill, New York (1954); *Proc. Geneva Conf.* Paper P/728 (1955).*
[4] E. K. HYDE and G. T. SEABORG *Handbuch der Physik* Vol. 39. Lange and Springer, Berlin (to be published).
[5] W. L. LATIMER *Oxidation Potentials* (Second Edition). Prentice-Hall, New York (1952).
[6] J. RYDBERG and B. RYDBERG *Ark. kemi* **9**, 81 (1956).

Mixtures of uranium and plutonium were obtained by neutron irradiation of UO_3. The product was dissolved in hot HNO_3, giving mainly U(VI) and Pu(IV) nitrates. Plutonium was isolated from the solution according to procedures described elsewhere.[7] On heating such solutions in 10M HNO_3, most of the plutonium is assumed to be converted to Pu(IV).[1] Higher oxidation states of plutonium were prepared by diluting this solution to make it 1M in HNO_3 and 0·1M in BrO_3^- and then heating to 95°C for 30 min. A test of the oxidation efficiency showed that the amount of Pu(IV) had decreased from 74 per cent to 1·4 per cent. The solutions thus obtained will be denoted Pu(VI) in the following. The concentration of plutonium in the experiments never exceeded 10^{-5}M.

The organic solvent, methyl *iso*butyl ketone (hexone), was of technical quality. It was washed thoroughly with alkali, acid, and finally water until a neutral pH was obtained. All other chemicals were of analytical grade.

Analysis

Total uranium was determined spectrophotometrically by the thiocyanate method.[8] The tetravalent uranium was determined either by precipitating with oxalic acid and weighing the precipitate,[6] or spectrophotometrically at 6550 Å. (At the same time U(VI) was determined at 4100 Å; in both wavelength regions corrections had to be applied for the other uranium species present.) The spectrophotometric investigations were made with a Beckman DU spectrophotometer.

Plutonium was determined by α-counting in an internal gas-flow proportional counter (Nuclear Measurements Corp., Indianapolis).

When Pu(IV) had to be determined, it was separated from the other valency states of plutonium by making the aqueous solution 1M in HNO_3 or $HClO_4$ and extracting with 0·3 M thenoyltrifluoroacetone (TTA) in benzene. Under these conditions, practically all Pu(IV) is extracted (~99·9 per cent; see further below) but no other plutonium species.[9]

RESULTS AND DISCUSSION

Stability of U(IV) Solutions

Solutions of U(IV) are fairly stable in the presence of certain strong acids or strongly complexing agents, if precautions are taken to avoid unnecessary oxidation.

Solutions of 0·1M U(IV) in 1M $HClO_4$, and in 1M HCl, have been kept for months in the dark and under an N_2 atmosphere at 20°C with no more than a few per cent oxidation; however, if the U(IV) concentration is much decreased, e.g. to 0·001M, fairly rapid oxidation can be observed and may amount to 10 per cent or more in an hour.[6] U(IV) is reported to show no oxidation within 4 hr in 1M H_2SO_4 at room temperature.[10] Benzene solutions of UAa_4, where Aa^- indicates an acetylacetonate ion, have been kept for several weeks without any noticeable oxidation.[6]

In the presence of nitrate ions, U(IV) is rapidly oxidized. This is illustrated by Fig. 1, which records two different types of experiments. In experiment *A* (full line), the original composition of the solution was 0·095M U(IV), 1M HNO_3 and 0·3M $HClO_4$; the solution was kept at 25°C in an N_2 atmosphere. The composition of the original aqueous solution in experiment *B* (broken line) was 0·26M U(IV), 0·25M U(VI), 0·7M HNO_3, and 3M $Ca(NO_3)_2$; this solution was then shaken in air with an equal volume of hexone, which had previously been equilibrated with HNO_3 (the hexone phase was then 1·06M in HNO_3).[11] Since the distribution factors for both U(IV) and U(VI) are about 10 under these conditions, about 90

[7] J. RYDBERG *Acta chem. scand.* **9**, 1252 (1955).
[8] C. J. RODDEN and J. C. WARF *Analytical Chemistry of the Manhattan Project* Chap. 1. N.N.E.S. Vol. VIII-1. McGraw-Hill, New York (1950); B. HÖK *Svensk kem. Tidskr.* **65**, 105 (1953).
[9] J. G. CUNNINGHAME and G. L. MILES *J. inorg. nucl. Chem.* **3**, 54 (1956).
[10] G. B. F. LUNDELL and H. B. KNOWLES *J. Amer. chem. Soc.* **47**, 2637 (1925).
[11] J. RYDBERG and B. BERNSTRÖM *Acta chem. scand.* **11**, 86 (1957).

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per cent of the uranium was transferred into the hexone phase.[11] The analyses for the oxidation of U(IV) were therefore made in the hexone phase in experiment *B*.

It would be expected that U(IV) would be more rapidly oxidized in experiment *B*, since in that case the solutions were in contact with oxygen all the time. However, the fact that most of the U(IV) is in the organic phase may lessen the rate of oxidation. No attempt was made to distinguish between these two effects. The net result is that in experiment *B*, U(IV) is slightly more rapidly oxidized than in *A*. After half an hour about 75 per cent of the U(IV) is still left.

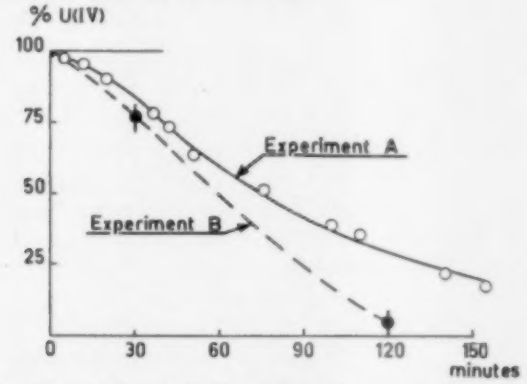

FIG. 1.—The reduction of U(IV) in HNO_3 solutions as a function of time (for details of experiments *A* and *B*, see text).

Reduction of Pu(IV) *and Pu*(VI) *in* HNO_3 *Solutions*

Plutonium solutions containing mainly ($\geq$74 per cent) Pu(IV) were added to solutions of 10–0·1M HNO_3 and 0·1–0·01M U(IV). The solutions were then analysed for Pu(IV) at different time-intervals between 2 and 30 min. The results indicated that 90 per cent of the Pu(IV) had been reduced. The best reduction was obtained $\sim$1M HNO_3 and at the higher U(IV) concentration, where >99 per cent had been reduced. No systematic trend with time could be detected.

The investigations on the reduction of oxidized plutonium were carried out in 1M HNO_3. Since the oxidized plutonium solutions contained BrO_3^- ions, U(IV) was added in excess over the BrO_3^- ions to make the solutions $\sim$0·1M in U^{4+}. Because of the oxidation of some of the U(IV), the solutions also contained a certain amount of UO_2^{2+} ions.

After 5–30 min, La^{3+} carrier and oxalic acid were added. The oxalate precipitate of U(IV) and La(III) carries quantitatively all Pu(IV) and Pu(III).[4] The U(VI) present acts as a hold back carrier. Since less than 0·1 per cent of U(VI) is precipitated under these conditions,[6] the amount of Pu(VI) in the precipitate is assumed to be negligible. It is also assumed that no Pu(V), if present, is precipitated by oxalic acid.[12]

The supernatant liquid and the precipitate were analysed for plutonium. Since <1 per cent plutonium was found in the supernatant liquid, Pu(VI) must have been reduced to either Pu(IV) or Pu(III).

In order to test which was the case, parallel runs were made where the solutions were analysed for Pu(IV) by the TTA extraction method instead of precipitating

[12] D. M. GRUEN and J. J. KATZ *J. Amer. chem. Soc.* **75**, 3772 (1953).

with oxalic acid. Less than 1 per cent plutonium could be detected in the extracts, indicating a >99 per cent reduction of plutonium to Pu(III). The results were independent of time between 5 and 30 min.

Reduction of Pu(IV) and Pu(VI) Nitrates in Organic Solvents

In order to test the efficiency by which plutonium could be reduced and stripped down from an organic solvent to an aqueous solution containing U(IV) and HNO_3 in the absence of strong complexing ligands (cf. next section), the experiments below were carried out. For comparison two other reductants were also used, namely ferrous hydroxylamine and sulphamate.

A hexone solution of plutonium was prepared by equilibrating an aqueous phase containing tracer plutonium, 0·04M UO_2^{2+}, 0·7M HNO_3, and 3M $Ca(NO_3)_2$, with a hexone phase, which had previously been made 1M in HNO_3. The plutonium in the hexone solution obtained consisted of ≥85 per cent Pu(IV) and ≤15 per cent Pu(VI).

This hexone solution was then equilibrated with a new aqueous solution, which was 0·7M in HNO_3, 3M in $Ca(NO_3)_2$, and contained the reductant. Both phases were then analysed for uranium, plutonium, and HNO_3. The results are given in Table 1.

Under the conditions used, the distribution factor of Pu(VI) is 13, of Pu(IV) 9,[11] and of Pu(III) probably <0·001 (cf. refs. 4 and 11). Thus most of the Pu(VI) and Pu(IV) will stay in the organic phase, while practically all Pu(III) goes into the aqueous phase. No attempt to distinguish between Pu(IV) and Pu(VI) has been made in the analyses, but in order to correct for the equilibrium concentration of these two species in the aqueous phase, an average distribution factor of 10 has been assumed for both. The error due to this simplification is negligible.

The percentage of reduced plutonium given in Table 1 is in some cases fairly uncertain; however, it is obvious that U(IV) in an oxygen free atmosphere is superior to ferrous sulphamate and hydroxylamine under the conditions used. In the presence of oxygen it is about as good as the other reducing agent.

The following experiment was carried out in order to test the stripping efficiency of U(IV) on pure Pu(VI).

An aqueous Pu(VI) solution in 1M HNO_3 and 2M $Mg(NO_3)_2$ was extracted with diethyl ether. The extraction of Pu(VI) is almost quantitative, while practically no Pu(III) or (IV) is obtained in the organic phase.[3,4,13] This organic solution was then equilibrated in an N_2-atmosphere with a similar aqueous solution which in addition contained 0·1M U(IV). The amount of plutonium in the organic phase, which can be regarded as equal to the total amount of Pu(VI) in the system, was then determined at different times. After 5 min the amount of U(VI) had decreased to 16 per cent, after 10 min to 4 per cent, and after 30 min to <1 per cent. The accuracy in these determinations is not better than a factor 2, but the results clearly indicate that plutonium is effectively stripped into the aqueous phase.

Reduction of Pu(IV) Bound as a TTA-Complex in Benzene

The over-all reaction for the complex formation and extraction of a metal ion (M^{N+}) with a chelating agent (e.g. the monobasic acid HA) can be written

$$M^{N+}(aq) + N\,HA(org) \rightleftharpoons MA_N(org) + N\,H^+(aq), \qquad (3)$$

N. N. HELLMAN and M. I. WOLF *U.S.A.E.C. Rep.* CB-3664 (1946).

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TABLE 1.—THE STRIPPING OF Pu(IV) AND Pu(VI) FROM HEXONE SOLUTION INTO AN AQUEOUS SOLUTION CONTAINING A REDUCING AGENT AT ROOM TEMPERATURE

Reducing agent	Equilibration time (min)	Organic phase			Aqueous phase				Reduced Pu (%)
		HNO_3 (mole/l.)	U (mole/l.)	Pu (c.p.m./0·1 ml)	HNO_3 (mole/l.)	U (mole/l.)	Pu(IV) + Pu(VI) (c.p.m./0·1 ml)	Pu(III) (c.p.m./0·1 ml)	
0·05M NH_2OH HCl	5	1·02	0·013	393 ± 40	0·70	0·0010*	39 ± 4	125 ± 120	20 ± 19
0·05M NH_2OH HCl	20	1·04	0·013	413 ± 40	0·7*	0·0010*	41 ± 4	30 ± 120	<27
0·05M NH_2OH HCl + 0·005 M Fe^{2+}	5	1·06	0·013	313 ± 40	0·71	0·0010*	31 ± 4	4 ± 15	<6
0·05M NH_2OH HCl + 0·005 M Fe^{2+}	5	1·04	0·012	250 ± 32	0·71	0·0010*	25 ± 3	530 ± 120	65 ± 8
0·05M $H_4NOSO_2NH_2$ + 0·005 MFe^{2+}	20	1·04	0·013	223 ± 33	0·71	0·0010*	22 ± 3	676 ± 44	74 ± 8
0·05M $H_4NOSO_2NH_2$	20	1·04	0·013	433 ± 40	0·7*	0·0010*	43 ± 4	105 ± 120	<34
0·05M $H_4NOSO_2NH_2$ + 0·005 M Fe^{3+}	5	1·17	0·013	304 ± 40	0·84	0·0010*	30 ± 4	−9 ± 14	<3
0·05M $H_4NOSO_2NH_2$ + 0·005 M Fe^{2+}	5	1·04	0·012	259 ± 32	0·7*	0·0010*	26 ± 3	610 ± 120	65 ± 10
0·05M $H_4NOSO_2NH_2$ + 0·005 M Fe^{2+}	20	1·04	0·013	322 ± 32	0·70	0·00108	32 ± 3	374 ± 34	52 ± 5
0·05M U^{4+} in air	5	1·12	0·021	157 ± 44	0·72	0·0036	16 ± 4	598 ± 35	70 ± 10
0·05M U^{4+} in N_2	5	1·09	0·027	19 ± 35	0·70	0·0017	2 ± 4	890 ± 34	95 ± 3

* Calculated, not measured.

where "aq" stands for the aqueous phase and "org" for the organic phase. If it is assumed that the only species of the metal in the aqueous phase is M^{N+} and in the organic phase MA_N, the distribution ratio q of the metal between the organic and aqueous phases will be

$$q = [MA_N]_{org}/[M^{N+}]_{aq}. \quad (4)$$

The equilibrium constant k for reaction (3) will consequently be given by

$$q = k([HA]_{org}/[H^+]_{aq})^N. \quad (5)$$

It can be shown that the assumption made here never holds exactly,[14] but equation (5) is often a useful approximation.

For the reaction between plutonium and TTA in a benzene-water system, CUNNINGHAME and MILES[9] have determined k for the different plutonium valency states: $k_{Pu(III)} \sim 3$, $k_{Pu(IV)} \sim 10^5$, and $k_{Pu(VI)} \sim 0{\cdot}1$. For $k_{U(VI)}$ they give an approximate value about equal to $k_{Pu(VI)}$.

By measuring q at various H^+ and HA concentrations, the author obtained for Pu(IV) and U(IV) the values $k_{Pu(IV)} = 10^{5{\cdot}3}$ and $k_{U(IV)} = 10^{\sim 3{\cdot}8}$. The former value is in good agreement with that given above,[9] while the latter is not far from that which can be calculated for U(IV) from data given by BETTS and LEIGH[15] ($k_{U(IV)} = 10^{5 \pm 1}$).

Using these values, the distribution ratios q of plutonium and uranium in a TTA-benzene-water system can be calculated as a function of $[HA]_{org}/[H^+]_{aq}$. It can be seen that if Pu(IV) is reduced to Pu(III), the plutonium will be stripped into the aqueous phase ($k_{Pu(III)}([HA]_{org}/[H^+]_{aq})^{-3}$ is generally $\ll k_{Pu(IV)}([HA]_{org}/[H^+]_{aq})^{\times 4}$); the stripping efficiency depends on the value of $[HA]_{org}/[H^+]_{aq}$.

The reduction of Pu(IV) by U(IV) in the two-phase system consisting of 0·1M TTA in benzene and 0·33M $HClO_3$ in water has been investigated as a function of time and U(IV) concentration. The results are given in Table 2.

For the lowest U(IV) concentration (0·01M), it can be calculated that ≥ 90 per cent of the U(IV) will be complexed by TTA. The concentration of free TTA in the organic phase will thus drop to about 0·06M, and the H^+ concentration of the aqueous phase increase to 0·37M. With these values, $k_{Pu(IV)}$, $k_{Pu(III)}$, and measured values of q_{Pu}, the amount of Pu(III) can be calculated using equation (5). Column 9 of Table 2 shows that in the presence of 0·01M U(IV), plutonium is slowly reduced to Pu(III). The reduction seems to be quantitative within 100 hr.

At the higher U(IV) concentrations, all the TTA can theoretically be used up by U(IV), thus lowering $[HA]_{org}/[H^+]_{aq}$ to such an extent that a considerable part of Pu(IV) is transferred into the aqueous phase (cf. equation 5). The concentration of Pu(III) cannot be calculated unless $[HA]_{org}$ is known, and $[HA]_{org}$ cannot be determined with any accuracy if the complex formation constants for the Pu(IV)-, Pu(III)-, and U(IV)-TTA complexes are unknown, which they are. Thus the last column in Table 2 only gives the amount of plutonium stripped into the aqueous phase, which depends on U(IV) either reducing Pu(IV) or expelling Pu(IV) from its TTA complex.

The slow reduction of Pu(IV) is probably due to the fact that the redox reaction takes place between the uncomplexed (hydrated) ions, according to equation (1),

[14] J. RYDBERG *Ark. kemi* **8**, 101, 113 (1955); *Rec. trav. chim.* **75**, 737 (1956).
[15] R. H. BETTS and R. M. LEIGH *Canad. J. Res.* **28B**, 514 (1950).

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TABLE 2.—THE REDUCTION OF Pu(IV) BY U(IV) IN A TWO-PHASE LIQUID-LIQUID SYSTEM. Pu(IV) ORIGINALLY PRESENT AS $Pu(TTA)_4$ IN 0·1M TTA IN BENZENE, AND U(IV) ORIGINALLY PRESENT IN 0·33M $HClO_4$

U(IV) (mole/l.)	Time	Organic phase			Aqueous phase			Reduced or stripped Pu(%)
		[U] (mole/l.)	[Pu] (c.p.m./0·1 ml)	[Pu(III)] (c.p.m./0·1 ml)	[U] (mole/l.)	[Pu] (c.p.m./0·1 ml)	[Pu(III)] (c.p.m./0·1 ml)	
1	2	3	4	5	6	7	8	9
0	5–30 min	—	6410 ± 100	<1	—	8 ± 2	<0·1	<0·1
0·010	5 ± 1 min	0·0081	5951	14	0·0024	224	196	3·2 ± 0·5*
	30 min	0·0081	5792	16	0·0024	932	905	14 ± 1*
	2·0 hr	0·0079	4025	20	0·0024	1112	1093	22 ± 1*
	5·5 hr	0·0074	3962	28	0·0023	1566	1548	29 ± 2*
	22 hr	0·0062	2187	52	0·0024	2889	2879	58 ± 3*
	32 hr	0·0055	2477	56	0·0025	3099	3087	56 ± 3*
	55 hr	0·0052	1188	82	0·0026	4587	4581	81 ± 5*
	83 hr	0·0055	356	100	0·0026	5551	5549	96 ± 8*
0·033	5 ± 1 min	0·021	5863	—	0·015	4431	—	7 ± 1†
	10 min	0·020	5683	—	0·015	840	—	15 ± 2†
	30 min	precipitate						
0·10	5 ± 1 min	0·021	4050	—	0·080	872	—	18 ± 2†
	10 min	0·018	4243	—	0·078	1387	—	25 ± 2†
	30 min	precipitate						

* Pu reduced. † Pu reduced and stripped.

and that in the presence of an excess of TTA, the concentration of free Pu^{4+} and U^{4+} ions in the aqueous phase is extremely small. In order to be reduced, practically all the Pu(IV) has to pass through the steps $Pu(TTA)_4(org) \rightarrow Pu(TTA)_4(aq) \rightarrow Pu(TTA)_3^+ \rightarrow Pu(TTA)_2^{2+} \rightarrow Pu(TTA)^{3+} \rightarrow Pu^{4+}$, and U(IV) has to pass a similar chain to be oxidized. It follows that the rate of reduction of Pu(IV) will increase with increasing U(IV) concentration (which is indicated by the results in Table 2), increasing acidity, and decreasing TTA concentration (cf. equation 5).

The Use of U(IV) in Processes for Separating Plutonium from Uranium

Most of the reducing agents which have been described [2,3] cf. also (ref.1) for the purpose of separating uranium from plutonium in a liquid-liquid extraction process introduces "foreign" substances into the system, as, e.g., cations like $Fe^{\times 2+}$ or anions like SO_4^{2-}, which might disturb or complicate the subsequent purification steps. Since the conditions can easily be chosen so that the tetra- and hexa-valent actinides prefer the organic phase, while the trivalent actinides go into the aqueous phase[11, 16-18], the net result of using U(IV) as a reducing agent for plutonium is an aqueous phase containing practically only plutonium (as Pu(III)), and an organic phase containing only uranium (as U(IV) *and* U(VI)). The plutonium solution thus obtained is very clean, and no problems of removing products of "foreign" reductants appear.

If the extraction can be carried out in solution free of NO_3^- ions[19], the increased stability of U(IV) is still more advantageous. However, it has been pointed out above, that if strong complexes are formed between Pu(IV) or U(IV) and an ion in the aqueous phase, the rate of reduction of plutonium may be slow. This is especially true in the presence of chelating agents, which practically all form strong complexes with tetravalent metal ions[20]. Since the solubility of metal chelate complexes in organic solvents practically never exceeds 0·1M (cf. Table 2), the use of organic complex formers is generally limited to dilute solutions of the metals.

Acknowledgement—The author wishes to thank the head of FOA 1, Prof. G. LJUNGGREN, for his kind support of this work, and Mrs. B. OLAUSSON for carrying out most of the experiments.

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ADSORPTION AND SOLVENT EXTRACTION PROCEDURES FOR THE SEPARATION OF CARRIER-FREE INDIUM FROM CADMIUM*

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(*Received* 4 *March* 1957)

Abstract—Procedures are given for the rapid separation of tracer quantities of indium from macro amounts of cadmium by adsorption and extraction techniques. The indium is adsorbed on to glass, paper, or cellulose ester fibres from ammoniacal solution and is extracted from buffered acetate solutions by 8-hydroxyquinoline in chloroform.

THE separation of carrier-free indium from other elements by means of isotopic and non-isotopic precipitates has been reported by several investigators.[1–5] Other separation techniques include selective elution from an ion-exchange column[6] and isolation after the (n,γ) recoil process from the metal phthalocyanine complex.[7] The object of the present work was to investigate the applicability of adsorption and extraction techniques for the separation of indium from cadmium. The adsorption of indium from ammoniacal solutions onto Pyrex glass, paper, and Millipore filters has been studied as a function of ammonium hydroxide concentration, cadmium ion concentration, temperature, and amount or porosity of adsorbent. The extraction of indium from buffered acetate solutions by 8-hydroxyquinoline in chloroform has been studied as a function of pH, cadmium ion concentration, and indium ion concentration. On the basis of these adsorption and extraction studies, rapid separations of carrier-free indium from cadmium have been developed.

EXPERIMENTAL

Reagents and materials

Cadmium-115-*indium*-115 m *active solution.* Neutron-irradiated cadmium acetate dihydrate was dissolved in 0·2 M acetic acid or 0·035 M perchloric acid.

Carrier-free indium-115 m *stock solution.* Three ml of cadmium-115-indium-115 m active solution (in transient equilibrium), 0·2 M in acetic acid, was added to 0·300 g of powdered glass in a 15 ml Pyrex cone. Three ml of 4 M ammonium hydroxide was added and the mixture stirred for approximately 3–5 min, then centrifuged. After discarding the supernatant liquid, the powdered glass and walls of the cone were washed with 4 M ammonium hydroxide to remove any traces of cadmium adhering to the surface. The activity which remained on the glass surfaces was dissolved in 0·035 M

* This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission.

[1] E. JACOBI *Helv. phys. Acta* **22**, 66 (1949).
[2] H. LAURENT *J. Chim. phys.* **48**, 412 (1951).
[3] L. GLENDENIN *Radiochemical Studies: The Fission Products* National Nuclear Energy Series, Div. IV. Vol. 9. p. 1575. McGraw-Hill, New York (1951).
[4] R. D. MAXWELL, H. R. HAYMOND, W. M. GARRISON, and J. G. HAMILTON *J. chem. Phys.* **17**, 1005 (1949).
[5] K. KIMURA and N. IKEDA *J. sci. Res. Inst. Tokyo* **45**, 128 (1951).
[6] K. A. KRAUS, F. NELSON, and G. W. SMITH *J. phys. Chem.* **58**, 11 (1954).
[7] W. HERR *Z. Naturf.* **76**, 201 (1952).

perchloric acid and its decay followed for 40 hr. No cadmium contamination was detected and the measured half-life of the isolated activity was 4·5 hr, in satisfactory agreement with previously reported values.[8]

Chloroform, analytical-grade reagent, was further purified according to the method of FIESER.[9]

Inactive indium solutions. Anhydrous indium trichloride was dissolved in hydrochloric acid and hydrous indium oxide precipitated from the solution with ammonium hydroxide. The hydrous oxide was washed thoroughly and ignited to constant weight. Solutions were prepared by dissolving the resulting oxide in perchloric acid.

Other reagents, analytical grade, were used without further purification. Solutions of inactive cadmium were prepared by dissolving hydrated cadmium chloride in 0·035 M perchloric acid.

Powdered glass. Pieces of Pyrex tubing were powdered, then screened. The 200$^+$-mesh fraction was purified by washing with 5–9 M hydrochloric acid, chromic acid cleaning solution, ethanol, and water. The purified glass was dried for approximately 12 hr at 110°C, then stored over Drierite.

Glass adsorption vessels. Fifteen ml Pyrex cones were cleaned by soaking overnight in concentrated nitric acid, then washing with distilled and redistilled water. The cones were air-dried before use in the adsorption experiments.

Other glass vessels used for adsorption were fritted-disc Pyrex funnels of fine, medium, and coarse porosity. These funnels were cleaned in the same manner as the cones, but were dried in an oven at 110°C.

Paper mash. Three circles of Whatman No. 42 (7·0 cm) filter paper were cut into small pieces and stirred with 50 ml of distilled water until completely disintegrated. The final volume of the mash was brought to 100 ml with water.

Other papers used for adsorption were 1-in. circles of Whatman No. 42 and Whatman No. 50 filter paper.

Millipore filters. VF and PH white, plain filters, 1 in. in diameter, were secured from Millipore Filter Corporation, Watertown, Massachusetts.

Extraction vessels. Ten ml Pyrex cones fitted with ground-glass stoppers were used in the extraction procedures.

Adsorption technique

Two types of adsorption experiments were employed for this study. In the first type, the adsorbing surface was the walls of a Pyrex cone, either alone or with added powdered glass or paper mash. In the second type, the absorbing surface was a fritted-glass disc funnel, Whatman filter paper, or a Millipore filter. In the experiments utilizing paper or Millipore filters as adsorbents, the filters were clamped between a ground-edge glass chimney, 89 mm high and 18 mm in diameter, and a Hirsch funnel without sides and with its surface ground flat.

Adsorption procedure—Type I. Five ml of an active indium solution, 0·035 M in perchloric acid, and of known inactive cadmium ion concentration, was added to 5 ml of ammonium hydroxide of the appropriate strength. The mixture was stirred in contact with the absorbing surface for 10 min, and then centrifuged for 10 min. The percentage indium adsorbed was calculated from the activity of the supernatant liquid. In over 95 per cent of the experiments, the activity adsorbed was removed from the surface with 5 M hydrochloric acid and counted. In those instances where cadmium was added, the adsorbent was washed once with 5 ml of ammonium hydroxide. The total activity recovered was always equal to at least 96 per cent of the initial amount used.

Adsorption procedure—Type II. Three to five ml of 10·7 M ammonium hydroxide was pipetted onto fritted-glass disc funnels, filter papers, or Millipore filters of different porosities. An equal volume of carrier-free indium-115 m in 0·035 M perchloric acid was added. The solutions were mixed by air-stirring momentarily with a capillary pipette and then filtered with suction. After washing the filters with 10 ml of 10·7 M ammonium hydroxide, the adsorbed activity was dissolved in 5–10 M hydrochloric acid and measured.

Extraction technique. An aliquot of carrier-free indium-115 m stock solution was adjusted to the appropriate pH by the addition of sodium acetate solution. In some instances, known amounts of inactive cadmium or indium were also added; the final volume being 4 ml in all cases. The aqueous

[8] R. P. METCALF *Radiochemical Studies: The Fission Products* National Nuclear Energy Series, Div. IV. Vol. 9. p. 898. McGraw-Hill, New York (1951).

[9] L. F. FIESER *Experiments in Organic Chemistry* (Second Edition) p. 365. D. C. Heath and Company, New York (1941).

solution was vigorously shaken with 4 ml of a 0·01 M solution of 8-hydroxyquinoline in chloroform for 5 min. After centrifuging at low speeds for approximately 2 min, the layers were separated; in the cases where cadmium was added, the organic layer was washed once with an aqueous solution of the same pH used in the initial extraction. The activity of each layer was determined.

Tests for cadmium contamination. The extent of co-separation of cadmium with the indium was determined by carrying out the adsorption or extraction procedures with solutions containing 2·33-day cadmium-115; the cadmium concentration, in all instances, was 0·01 molar. The radiochemical contamination of the separated activity was determined from decay curves which were obtained over a period of 30–45 hr. The gross cadmium contamination was determined by comparing the colour developed when hydrogen sulphide was passed through a slightly alkaline solution of the separated activity with that developed in a set of standard cadmium solutions. In the extraction experiments, the indium was recovered from the chloroform layer by extraction with an equal volume of 1 M nitric acid. The hydrogen sulphide tests were conducted on the active solution after destruction of the 8-hydroxyquinoline with a sulphuric acid–perchloric acid mixture. The lower limit of cadmium detection by the hydrogen sulphide method used was 2×10^{-7} M.

Measurement of radioactivity. Liquid samples of active indium or cadmium were prepared for counting by dilution with 5–10 M hydrochloric acid to a standard height in calibrated Pyrex tubes. The γ rays associated with the decay of cadmium-115 and indium-115m were detected with a scintillation counter employing a No. 5819 RCA phototube and a thallium-activated sodium iodide crystal.

RESULTS AND DISCUSSION

The results of adsorption experiments of Type I are summarized in Figs. 1–3. These results suggest that maximum adsorption occurs from solutions which are 2–5·3 M in ammonium hydroxide and $\leqslant$0·01 M in cadmium ion. Powdered glass

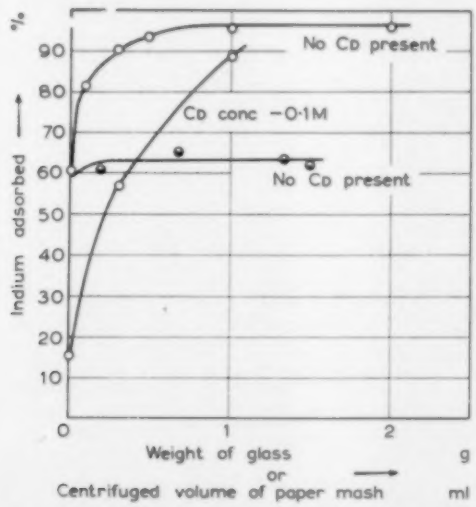

Fig. 1.—Adsorption of carrier-free indium at room temperature from 5·33 M ammonium hydroxide as a function of amount of adsorbent.
Adsorbents ○ Pyrex cone + powdered glass
◒ Pyrex cone + paper mash

was more effective than paper mash. Although the data indicate the use of 0·5–2·0 g of powdered glass, it was found advantageous to use 0·3 g in order to avoid excessive volumes of wash solution. Using the best conditions indicated for each of the three adsorbing surfaces, the tests for radiochemical contamination were negative except

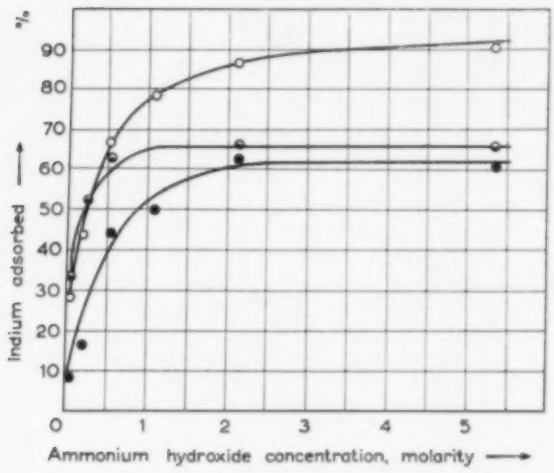

FIG. 2.—Adsorption of carrier-free indium at room temperature as a function of ammonium hydroxide concentration. No cadmium present.
Adsorbents ○ Pyrex cone + 0·300 g powdered glass
◒ Pyrex cone + 0·69 ml paper mash
● Pyrex cone

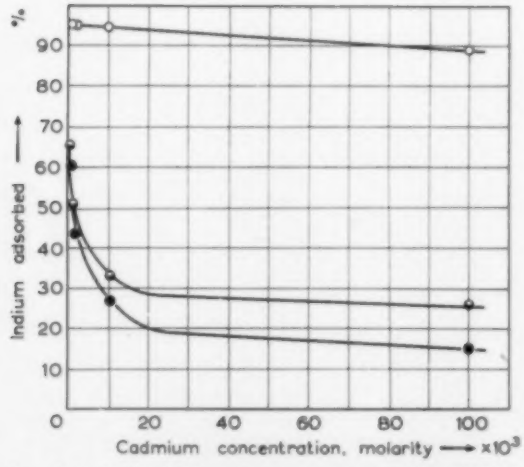

FIG. 3.—Adsorption of carrier-free indium at room temperature from 5·33 M ammonium hydroxide as a function of cadmium concentration.
Adsorbents ○ Pyrex cone + 1·000 g powdered glass
◒ Pyrex cone + 0·69 ml paper mash
● Pyrex cone

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for the experiments employing paper mash. In this case the gross cadmium contamination, estimated from the decay curve, was ~0·5 per cent and may be attributed to difficulties encountered in completely washing the mash. The gross cadmium contamination, determined by the hydrogen sulphide test, for experiments using Pyrex cones plus 0·3 g of powdered glass as adsorbent, was 0·2 per cent after one wash with ammonium hydroxide. This amount of contamination can be reduced to <0·002 per cent with a second ammonium hydroxide wash, but is accompanied by a reduction in yield from 91 per cent to 72 per cent. This adsorption procedure is adaptable to larger-scale separation. An experiment carried out at the temperature of a steam bath showed only a slight increase (~1 per cent) in the percentage of indium adsorbed.

The results of Type II adsorption experiments are summarized in Table 1. The amount of indium adsorbed on the fritted-glass disc is a function of both the flow-rate of the solution and the porosity of the disc. Essentially quantitative adsorption is

TABLE 1.—ADSORPTION OF INDIUM ON FRITTED-GLASS DISCS, MILLIPORE FILTERS, AND WHATMAN FILTER PAPERS

Type of adsorbent	Porosity	Flow-rate (ml/sec)	Indium adsorbed (per cent)
Fritted-glass discs	Fine	0·09	94—99
	Medium	0·2 0·3	90 30—50
	Coarse	0·8 0·3[a]	40 32—53
Millipore filters	300 mμ	0·3	15
	10 mμ	0·03	18
	10 mμ	0·03[b]	30
	10 mμ	0·03[c]	17
Whatman papers	No. 50	0·3	<4
	No. 42	0·3	<4

[a] Suction was not applied.
[b] The solution was allowed to stand on the filter 5 min, with stirring, prior to filtration.
[c] The solution was allowed to stand on the filter 10 min, with stirring, prior to filtration.

effected on discs of fine porosity. In cases where high yields are not of great importance, discs of medium and coarse porosities provide means of attaining 30–90 per cent adsorption in 10–50 sec. Increasing the cadmium concentration to 0·01 M does not alter the percentage of indium removed. Consequently, these adsorbents

may be used in effecting rapid separations of the two elements. With Millipore filters, 15–30 per cent carrier-free indium is adsorbed; however, from solutions which are 0·01 M in cadmium, the indium adsorption is reduced to approximately 4 per cent. Thus, under the conditions of these experiments, Millipore filters and Whatman filters proved to be much less effective for separation of indium from cadmium. The purity of the separated activity from fritted-glass discs and Millipore filters was high; no detectable contamination was revealed by analysis of the decay curves, and $<0{\cdot}002$ per cent cadmium was indicated by the hydrogen sulphide colour tests. No tests for cadmium contamination were made in the case of the Whatman filter papers.

The selective extraction of indium as 8-hydroxyquinolinate with chloroform has been developed by MOELLER[10] as a satisfactory means of separating indium in macro quantities from cadmium and other elements. This procedure has been applied in the present work to the separation of tracer amounts of indium from cadmium. In the pH range 3·4–6·4 the extraction of indium from aqueous solution is essentially quantitative. Varying the cadmium concentration from 10^{-1} to 10^{-3} M or the indium concentration from tracer amounts ($\sim 10^{-12}$ M) to 5×10^{-5} M, at a pH of 3·85, had no detectable effect on the percentage of indium extracted. No detectable amounts of radiocadmium were found in the carrier-free indium separated from solutions which were 0·01 M in cadmium and at a pH of 3·85. However, the gross cadmium contamination determined by the hydrogen sulphide method was $\sim 0{\cdot}5$ per cent after one aqueous extraction of the chloroform layer and $<0{\cdot}002$ per cent after a second extraction.

Acknowledgements—The authors wish to express their appreciation to Dr. G. A. COWAN and Mr. A. W. MILLER of the Los Alamos Scientific Laboratory for the irradiation of the samples of cadmium acetate dihydrate.

[10] T. MOELLER *Industr. Engng. Chem. (Anal.)* **15**, 207 (1943).

ERRATUM

J. inorg. nucl. Chem. **4**, 239 (1957).

P. KAFALAS and C. E. CROUTHAMEL: The absolute yield of ^{137}Cs in fast neutron fission of ^{235}U and ^{239}Pu

THE absolute fission yields reported by us in the previous issue of this journal have been found to be in error. The corrected fission yields of ^{137}Cs are $6{\cdot}30 \pm 0{\cdot}17$ per cent for ^{235}U and $6{\cdot}81 \pm 0{\cdot}20$ per cent for ^{239}Pu.

This error arose because of the instability of the carrier-free ^{137}Cs solution used to calibrate the counter. This tracer was a 2 M HCl solution of the carrier-free ^{137}Cs stored in a Pyrex bottle. An appreciable fraction of the activity (approximately 20 per cent) was deposited on the walls of the bottle during the one-month period that the counter was being calibrated for self-absorption and self-scattering. The counter has since been meticulously recalibrated, using a new tracer solution containing a small amount of cesium carrier (approximately 1 μg Cs /ml) in 2 M HCl. The activity of the new ^{137}Cs solution has remained stable for a period of several months.

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THE INDEPENDENT YIELDS OF ^{140}La, ^{90}Y, and ^{91}Y IN THE THERMAL NEUTRON FISSION OF ^{235}U and ^{233}U

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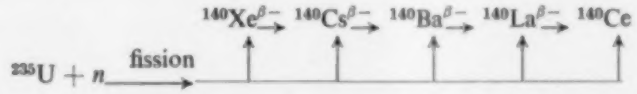
Abstract—The independent yields of ^{140}La have been radiochemically determined for the thermal neutron fission of ^{235}U and ^{233}U to be $4{\cdot}5 \times 10^{-2}$ per cent and $2{\cdot}4 \times 10^{-2}$ per cent respectively. A study of the hypotheses advanced to date concerning charge distribution in fission has indicated that the equal charge displacement postulate still gives the best agreement with experimental values, although additional data may prove this to be fortuitous. The ^{140}La yields are considerably lower than the values estimated from this postulate, as is to be expected for an 83 neutron configuration if closed shell species are favoured in the fission process.

An investigation of the apparent independent yield of ^{91}Y has produced evidence that some mechanism other than direct formation has contributed to the high yields observed.

Attempts have been made to measure the independent yield of ^{90}Y, and an upper limit of 4×10^{-4} per cent has been estimated for ^{235}U and ^{233}U fission. If, however, selectivity does exist in the region of closed shells, ^{90}Y yields much below these limits can be anticipated due to the effects of the 50 neutron shell.

THE total yield of any isobaric chain resulting from fission fragment decay (e.g. the mass 140 chain shown below) can be defined as the cumulative yield of the last member of the chain, or as the sum of the separate yields, at the instant of fission, of all the members of the chain. These separate, or primary, yields may be expressed either as independent fission yields (a percentage of the fissions which have occurred), or as a fraction of the chain yield for that particular mass number.



Since there is no direct evidence of the relative distribution of primary fission yields along a single chain of constant mass (i.e. the charge distribution), all correlations of measured yields made to date have been based on the assumption that the distribution is symmetrical and is independent of the charge and mass of the fissioning nucleus, the number of neutrons emitted and the division of mass in the fission process. Several hypotheses concerning charge distribution were proposed by early workers in this field, but it was shown by GLENDENIN, CORYELL, and EDWARDS[1] that the observed fractional yields agreed best with a postulate of equal charge displacement, which requires that the most probable mode of fission gives fragments with equal charge excess, i.e. equal effective chain lengths in subsequent β^- decay. If Z_p is defined as the most probable charge in fission giving rise to mass X, then a fairly smooth curve

[1] L. E. GLENDENIN, C. D. CORYELL, and R. R. EDWARDS *Radiochemical Studies: The Fission Products* (Ed. C. D. CORYELL and N. SUGARMAN) National Nuclear Energy Series, Div. IV, Plutonium Project Record. Vol. 9. Paper 52. McGraw-Hill, New York (1951).

of fractional chain yield plotted against displacement from the most probable charge ($Z - Z_p$) is obtained from this postulate, but deviations are observed in the region of closed shells.

PAPPAS,[2] and more recently STEINBERG and GLENDENIN[3] have replotted the data using later values for the fractional chain yields, and Z_p's calculated from the Z_A (most stable charge) values of CORYELL *et al.*[4] An allowance was introduced for the emission of prompt neutrons after the division of charge[2] by calculating the most probable charge, Z_p, for a chain of mass X, as follows; assume mass X is formed at the instant of charge division as $X+1$ with subsequent neutron emission; then use Z_A for $X+1$, rather than Z_A for X, to calculate Z_p for chain X. These refinements improve the agreement with a single curve, but at shell crossings the uncertainty at Z_A continues to make the estimation of Z_p inaccurate, and the postulate still makes little attempt to account for the probable influence of closed shells on Z_p. However, both GLENDENIN and PAPPAS have recognized that the fine structure in the cumulative yield data can be attributed to the effect of the 82 neutron shell, and that this may result in increased yields at neutron numbers 82, 84, and 86, with a corresponding decrease at 83, 85, and 87.

KENNETT and THODE[5] have suggested that these uncertainties can be removed if shell effects are taken into account in the evaluation of Z_p for any given mass, by using the criterion that the most probable Z is the one for which the prompt energy release in fission is a maximum. The shift in Z_p introduced in the region of a closed shell by this concept should be reflected in altered yields for all members of a nearby isobaric sequence, although the general shape of the distribution curve will be unchanged. They have calculated ($Z - Z_p$) for several modes of fission near the 50 proton and the 82 neutron shells, using the nuclear mass data of KUMAR and PRESTON,[6] and report that Z_p is shifted in a direction and by an amount sufficient to bring the ^{128}I and ^{130}I fractional yield measurements into line with one another.

It is obvious that a considerably larger body of experimental data must be collected in order to prove or disprove these hypotheses, and it was as a test of the equal chain length proposal that the present work was undertaken. The authors feel that the independent yields estimated in this work can provide some relevant information on this topic, since ^{140}La and ^{90}Y each have one neutron in excess of the closed shell configuration, while ^{91}Y has two neutrons in excess. In all cases there have been previous attempts to measure these yields in ^{235}U fission, and the following fractional chain yield limits have been reported: $^{140}\text{La} < 3 \times 10^{-2}$,[3] $^{90}\text{Y} < 5 \times 10^{-4}$,[3] and $^{91}\text{Y} < 9 \times 10^{-3}$,[7] but in no case was the nuclide observed.

EXPERIMENTAL

For the study of fission yields in ^{235}U, samples consisting of several milligrams of natural U_3O_8 were irradiated. Preliminary investigation of this material showed the presence of approximately one part per million of rare earth, from which ^{140}La and ^{90}Y could be produced by neutron capture.

[2] A. C. PAPPAS Technical Report No. 63, Laboratory for Nuclear Science, Massachusetts Institute of Technology (1953) (unpublished); *International Conference on the Peaceful Uses of Atomic Energy* Vol. 7, p. 19. (1955).
[3] E. P. STEINBERG and L. E. GLENDENIN *International Conference on the Peaceful Uses of Atomic Energy* Vol. 7, p. 3. (1955).
[4] C. D. CORYELL, R. A. BRIGHSTEN, and A. C. PAPPAS *Phys. Rev.* **85**, 732 (1952).
[5] T. J. KENNETT and H. G. THODE *Phys. Rev.* **103**, 323 (1956).
[6] K. KUMAR and M. A. PRESTON *Canad. J. Phys.* **33**, 298 (1955).
[7] G. W. REED *Phys. Rev.* **98**, 1327 (1955).

In order to reduce this to a negligible value the uranium was purified before irradiation, by extracting into tri-butyl phosphate from which it was recovered in a dilute ammonium carbonate wash, subsequently evaporated and ignited to U_3O_8. This procedure reduced the yttrium content of the sample from 0·85 μg/g to 0·01 μg/g uranium. No attempt was made to measure the lanthanum content after purification as, (a) it should have been reduced to the same extent as the yttrium by the solvent extraction and (b) a higher quantity could be tolerated.

^{233}U in solution as uranyl nitrate was transferred to a polythene capsule and evaporated to dryness before irradiation. In both cases the capsules were placed in a high flux position in the NRX reactor and removed rapidly at the end of one minute.

On dissolution samples were divided into 4 aliquots, and lanthanum and yttrium separated from the first two of these very soon after irradiation, while independent formation was still the chief contributor to these activities. Similar separations from the other 2 aliquots were deferred until many days after the irradiation, in order that the barium and strontium present could be determined by measuring their respective daughter activities after the residual independently formed lanthanum and yttrium activities had become insignificant in comparison with that formed by growth from the parent.

A detailed account of the radiochemical procedures used (precipitations, anion and cation exchange separations, etc.), is given in appendix A.

Samples were counted as soon as possible after preparation, while counting rates were of the order of 100 counts/min, and the decay followed for several days. The decay of 10 hr ^{90}Y and 57·5 day ^{91}Y was followed through 430 and 600 mg/cm^2 lucite absorbers in order to observe the ^{90}Y formed independently. At this level of activity it was necessary to use a low background G-M counter of the type described elsewhere.[8]

Blanks were done between experiments in order to check possible lanthanum and yttrium contamination of columns and glassware arising by decay from the relatively long-lived barium and strontium formed in a previous irradiation.

RESULTS

The measured counting rates were corrected for counter fluctuations, resolving time of the counter, and slight variations in mass thickness of the samples. The formulae derived for the calculation of fractional yields are given in appendix B.

Three determinations were made both for ^{235}U and ^{233}U, the results for ^{140}La being presented in Table 1, those for ^{91}Y in Table 2. The average of the observed fractional yields for ^{140}La is $7{\cdot}0 \times 10^{-4}$ for ^{235}U and $3{\cdot}8 \times 10^{-3}$ for ^{233}U fission, the increase being a result of the decreased mass/charge ratio in ^{233}U.

Inspection of the data of Table 1 for a single experiment has shown that the second extraction gave slightly higher results, but this difference is not apparent when the results are averaged by grouping together those separated at corresponding times (see Table 3). In preliminary runs considerable difficulty was experienced in achieving exchange in aliquot 1, particularly when appreciable nitrate was present, but this was overcome by the method outlined in appendix A. The apparent independent yield is, of course, extremely sensitive to the recovery of ^{140}La in aliquots 1 and 2, and presumably the observed differences result from slightly poorer exchange in the first extraction.

In contrast, the observed yield of ^{91}Y formed other than by decay of 9·7 hr ^{91}Sr shows an increase with time of separation (Table 2). The values for ^{235}U and ^{233}U fission are not substantially different (both being in the range of 0·005 to 0·02 when expressed as an apparent fractional yield). The equal charge displacement hypothesis would predict a much lower yield than this in ^{235}U fission (2×10^{-4} at mass 91, plus 1×10^{-3} if all of mass 92 feeds in), and in addition would predict a result approximately five times higher for ^{233}U than for ^{235}U fission. The observed similarity in ^{235}U and ^{233}U yields indicates that the measured ^{91}Y is not being formed directly in fission, and this suggestion is supported by an increase in yields with time of separation. The systematics in this region make the existence of nuclear isomerism in ^{91}Sr most probable, and the observed results could be explained if 0·02 of the chain decayed through an isomer with a half-life of about 0·5 hr. As the expected fractional chain yield at ^{91}Sr is about 0·05, the isomer could be formed directly in fission or result from the decay of ^{91}Rb.

The measurement of a fractional chain yield for ^{90}Y is made somewhat more difficult by the

[8] W. E. Grummitt, R. M. Brown, A. J. Cruikshank, and I. L. Fowler *Canad. J. Chem.* **34**, 206 (1956).

TABLE 1.—FRACTIONAL YIELDS OF ^{140}La

Fissioning nuclide	Run	t_1 (hr)	t_2 (hr)	N_{La} at t_2 (atoms)	N_{Ba} at t_1 (atoms)	Fractional yield $\times 10^4$
^{235}U	1	0·0167	0·724	1090	464,000	7·0 ± 0·9
^{235}U	2	0·0167	0·438	2670	1,944,000	3·7 ± 1·0
			0·685	4370	1,944,000	7·1 ± 0·9
^{235}U	3	0·0167	0·290	971	765,000	6·0 ± 0·5
			0·467	1370	765,000	7·3 ± 0·8
					Weighted Average =	7·0 ± 0·4
^{233}U	1	0·0167	0·330	3880	809,000	40 ± 2
			0·699	5190	809,000	49 ± 2
^{233}U	2	0·0333	0·521	4400	1,170,000	26 ± 2
			0·838	6430	1,170,000	37 ± 2
^{233}U	3	0·0167	0·332	4810	1,126,000	35 ± 2
			0·662	5060	1,154,000	41 ± 2
					Weighted Average =	38 ± 1

t_1 = irradiation time.
t_2 = time from end of irradiation to separation of La from Ba.

TABLE 2.—FRACTIONAL YIELD OF ^{91}Y

Fissioning nuclide	Run	t_1 (hr)	t_2 (hr)	N_Y at t_2 (atoms)	N_{Sr} at t_1 (atoms)	Fractional yield $\times 10^2$
^{235}U	3	0·0167	0·290	9,490	318,000	0·9 ± 0·2
	3	0·0167	0·467	14,800	318,000	1·1 ± 0·2
^{235}U	2	0·0167	0·685	74,000	1,347,000	0·8 ± 0·2
^{235}U	1	0·0167	0·724	9,750	150,000	1·5 ± 0·2
	1	0·0167	1·5	17,800	150,000	7·8 ± 0·4
^{233}U	1	0·0167	0·330	20,000	552,000	1·2 ± 0·2
^{233}U	3	0·0167	0·332	23,600	656,000	1·2 ± 0·2
^{233}U	2	0·0333	0·521	40,700	896,000	0·8 ± 0·3
^{233}U	3	0·0167	0·662	35,100	656,000	1·6 ± 0·3
^{233}U	1	0·0167	0·699	35,500	552,000	1·5 ± 0·3
^{233}U	2	0·0333	0·838	67,700	896,000	1·7 ± 0·3

t_1 = irradiation time.
t_2 = time from end of irradiation to separation of Y from Sr.

unexpectedly high ^{91}Y yield, as this appears as a background against which ^{90}Y must be measured. However, ^{91}Y can be discriminated against by the use of absorbers of sufficient thickness to stop most of its β^- rays, and a factor of 80 can be obtained with Lucite at 1/2 per cent counting efficiency for ^{90}Y. Careful analyses of decay curves taken with absorbers indicate limits of $< 8 \times 10^{-5}$ for the fractional chain yield of ^{90}Y in ^{233}U and ^{235}U fission.

DISCUSSION

In order to make any comparison of the observed primary yields of ^{140}La and ^{90}Y and those predicted by the equal charge displacement curve of GLENDENIN[1] it is first necessary to calculate the position in the chain, i.e. $(Z - Z_p)$, for these nuclides.

In the region of the 50 and 82 neutron shells, however, uncertainties in the values of Z_A due to shell crossings introduce an uncertainty of the order of $\pm 0{\cdot}5$ charge units in the calculated value of Z_p when substitution is made in the modified formula.[2] Some better method of estimating Z_p for masses 90 and 140 is desirable if the data are to contribute to an understanding of the fission process.

TABLE 3.—^{140}La FRACTIONAL YIELDS AS A FUNCTION OF THE SEPARATION TIME

	$t_{\frac{1}{2}}$ (hr)	Average fractional yield
^{235}U	0·290	$6{\cdot}0 \times 10^{-4}$
	0·438	$5{\cdot}5 \times 10^{-4}$
	0·467	
	0·685	$7{\cdot}0 \times 10^{-4}$
	0·724	
^{233}U	0·33	$3{\cdot}8 \times 10^{-2}$
	0·33	
	0·52	
	0·66	$3{\cdot}8 \times 10^{-3}$
	0·70	
	0·84	$3{\cdot}7 \times 10^{-3}$

Working from the experimental values compiled by WAPSTRA,[9] two calculations of mass excesses in the fission fragment region have recently been made: HAY and NEWTON[10] have extrapolated β^- decay Q values, while CAMERON[11] has determined new constants in a refined empirical mass formula. From these data Z_A, the charge associated with the maximum nuclear binding energy in an isobaric sequence, can be obtained by plotting mass excesses as a function of Z, and choosing that value of Z which yields $\frac{df(Z)}{dZ} = 0$. In calculating Z_p the method used[2] has been extended to allow for the non-integral average number of neutrons emitted per fission in ^{235}U, ^{233}U, ^{239}Pu and ^{242}Cm; e.g. for ^{235}U + thermal n $\rightarrow$ ^{140}La + Br + 2·5n

$$^{140}Z_p = 0{\cdot}75\left[{}^{141}Z_A - \left(\frac{{}^{141}Z_A + {}^{95}Z_A - 92}{2}\right)\right] + 0{\cdot}25\left[{}^{142}Z_A - \left(\frac{{}^{142}Z_A + {}^{94}Z_A - 92}{2}\right)\right]$$

assuming that 1·25 neutrons, with multiplicities 1 or 2, are released from each fragment after charge division has occurred. (The use of neutron emission probabilities calculated from simple evaporation theories[12] adjusted to fit the observed neutron multiplicity distribution was found to change Z_p by $<0{\cdot}05$ from the value obtained using this simple formula.)

[9] A. H. WAPSTRA *Physica* **XXI**, 385 (1955).
[10] I. W. HAY and T. D. NEWTON *Canad. J. Phys.* **35**, 195 (1957).
[11] A. G. W. CAMERON Physics Division, A.E.C.L. Private communication.
[12] R. B. LEACHMAN *Phys. Rev.* **101**, 1005 (1956).

In Fig. 1 the charge distribution curve has been constructed using the data of Table 4, $(Z - Z_p)$ values being obtained as outlined above. Recalculation of Z_p has not altered the shape or location of the distribution significantly. In general the reduction of the uncertainty in the abcissa has improved the agreement between observed and predicted yields, although certain yields are considerably displaced, presumably due to shell effects.

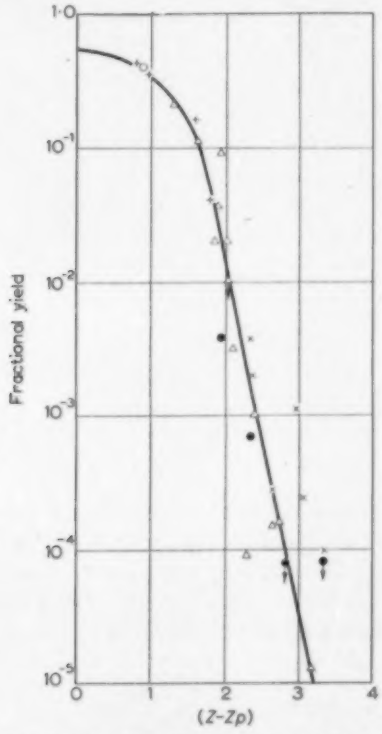


FIG. 1.—Fractional yields plotted against $(Z - Z_p)$ values derived by the equal chain length postulate. All data given in Table 4.
△ yields taken from STEINBERG and GLENDENIN,[3]
× yields reported by KENNETT and THODE,[5]
+ yields reported by WAHL,[14]
● yields reported in this paper,
○ yield predicted in this paper.

The yields recently measured for ^{128}I[5] would appear to represent the most serious challenge to the postulate of equal charge displacement, as on the average they lie 0·5 charge units from the curve even if one assumes that $^{128}Z_p$ is affected by the 50 proton shell and is in fact 50·0 $(Z - Z_p = 3{\cdot}0)$. KENNETT and THODE[5] have shown that the ^{128}I and ^{130}I results are compatible with one another if Z_p is approximately 50 for both chains, and that this is the case if Z_p is derived from the mass data of KUMAR and PRESTON[6] on the assumption that the associated energy release in fission is at a maximum.

It would be desirable to extend these calculations to include mass 140, as the independent yield of this chain might be similarly affected by nearby shells, but

TABLE 4.—INDEPENDENT YIELD DATA

Fissile nuclide	Fission product	Independent yield (%)[a]	Fraction of chain yield[b]	Position in chain ($Z - Z_p$)	
				Equal chain length postulate	Maximum energy release postulate
^{235}U thermal fission	^{79}As	1.8×10^{-3}	9.0×10^{-5}	1·96	1·25
	^{82}Br	3.5×10^{-5}	1.5×10^{-6}	2·65	1·59
	^{86}Rb	3.1×10^{-5}	1.3×10^{-5}	3·18	1·79
	^{90}Y	$<4.0 \times 10^{-4}$	$<8.0 \times 10^{-5}$	3·35	2·36
	^{96}Nb	5.7×10^{-4}	9.0×10^{-5}	2·30	2·31
	^{129}I	3.6×10^{-5}	9.8×10^{-5}	3·36	3·24
	^{130}I	4.5×10^{-4}	2.8×10^{-4} [d]	2·68	2·57
	^{132}I	$<4.4 \times 10^{-2}$	$<1.0 \times 10^{-2}$ [d]	2·06	1·76
	^{134}I	1·0	0·21[e]	1·31	1·01
	^{135}Xe	0·22	3.6×10^{-2} [c]	1·91	1·62
	^{136}Xe	3·4	0·57[f]	1·40	1·20
	^{136}Cs	6.2×10^{-3}	1.0×10^{-3} [d]	2·40	2·20
	^{137}Xe		(0·40)	0·90	
	^{140}La	4.5×10^{-2}	7.0×10^{-4} [g]	2·37	2·81
	^{141}La	0·1	2.0×10^{-2} [c]	1·87	2·56
^{235}U 14 MeV fission	^{131m}Te	1·6	0·35[e]	0·97	0·70
	^{132}I	0·8	0·16[e]	1·60	1·33
	^{134}I	2·5	0·43[e]	0·79	0·40
	^{136}Cs	~0·2	4×10^{-2} [h]	1·80	1·79
^{233}U thermal fission	^{90}Y	$<4.0 \times 10^{-4}$	$<8.0 \times 10^{-5}$	2·82	2·05
	^{132}I	1.9×10^{-4}	1.1×10^{-2} [c]	2·96	2·88
	^{130}I	4.3×10^{-3}	3.8×10^{-3} [d]	2·35	2·35
	^{136}Cs	0·12	2.0×10^{-2} [d]	2·04	1·86
	^{140}La	2.4×10^{-2}	3.8×10^{-3} [c]	1·96	2·42
^{239}Pu thermal fission	^{86}Rb	1.1×10^{-4}	1.6×10^{-6}	2·74	1·73
	^{132}I	2.0×10^{-4}	2.4×10^{-6}	3·07	2·91
	^{130}I	5.2×10^{-3}	2.0×10^{-3} [d]	2·38	2·29
	^{136}Cs	1.8×10^{-2}	3.1×10^{-3} [d]	2·11	1·82
^{242}Cm thermal fission	^{136}Cs	0·80	0·11	1·64	1·3

[a] All independent yields taken from a previous tabulation,[3] except where otherwise noted.
[b] All chain yields used in calculations taken from the smooth yield curves, except those reported by WAHL[14] for 14 MeV fission.
[c] Reported in this paper.
[d] Reported by KENNETT and THODE.[6]
[e] Reported by WAHL.[14]
[f] Average of yields reported by BROWN and YAFFE,[15] and KATCOFF and RUBINSON.[16]
[g] Difference between experimental and predicted values for ^{140}Xe.
[h] Measured by COMSTOCK, reported by FORD.[17]

[14] A. C. WAHL *Phys. Rev.* **99**, 730 (1955).
[15] F. BROWN and L. YAFFE *Canad. J. Chem.* **31**, 242 (1953).
[16] S. KATCOFF and W. RUBINSON *Phys. Rev.* **91**, 1458 (1953).
[17] G. P. FORD U.S.A.E.C. Report AECD 3597 (1953) (unpublished).

before attempting this it was essential to determine whether the fractional yield data at present available are compatible with the maximum energy release postulate. This required the calculation of Z_p for a range of fission product masses and fissile nuclides, a project which was greatly facilitated by recent estimations of energy releases in spontaneous fission.[10,11] A table of Z_p values and a corresponding plot of all fractional yields have been prepared and issued in a separate report[13] from which the data of column 5, Table 4 are taken.

TABLE 5.—CHAIN LENGTHS PREDICTED BY THE MAXIMUM ENERGY RELEASE HYPOTHESIS

Mass	Z_A	Z_p	Most probable chain length $(Z_A - Z_p)$
78	34·3	31·3	3·0
82	35·8	32·8	3·0
87	37·8	35·1	2·7
96	42·2	38·3	3·9
97	42·6	38·6	4·0
136	56·0	52·3	3·7
137	56·23	52·7	3·5
150	62·5	57·3	5·2
152	63·2	58·3	4·9

In contrast to the values calculated previously,[5] these results show only a slight 50 proton effect, and hence are very similar in the region of symmetrical fission to those obtained from the equal chain length postulate. In common with several others, the maximum energy release hypothesis in its present form predicts short chains in the light mass region and longer than average at high masses (Table 5). This appears to be in substantial disagreement with published results for ^{86}Rb, ^{78}As, ^{82}Br, ^{96}Nb, and ^{141}La, as well as with ^{90}Y reported here. As these yields, with the exception of the heavy group member ^{141}La, are considerably lower than those predicted, they are not likely to result from errors in measurement, e.g. radioactive contamination, neutron capture or isomerism.

However, these apparent differences in chain length could result from unsymmetrical charge distribution curves in the high and the low mass region. In that case one would expect high yields close to stability in the heavy group to be reflected in increased yields far from stability in the light group. Recent calculations by CAMERON[11] indicated that such asymmetries do exist in the energy release distributions, and although small, they appear to be in the right direction to account for the "altered chain lengths". For mass ratios near unity the charge distribution must of course be symmetric about the maximum, and both postulates give essentially the same $(Z - Z_p)$ values. If the charge distribution is indeed asymmetric for high mass ratios, then the yields in this region must lie on two curves, both different from that of the symmetric yields. However, by choosing a Z_p leading to equal chain lengths, rather that the Z_p defined on page 93, the conventional plot of GLENDENIN[1] should shift these

[13] W. E. GRUMMITT and GWEN M. MILTON *Chalk River Report CRC* 694 (1957).

two yield curves so that they overlap the one for the symmetric yields. It would, nevertheless, result in the light fragment yields lying above the heavy fragment yields for small $(Z - Z_p)$ values and below for very large $(Z - Z_p)$. The position of most of the data available is such that this effect would be nearly unnoticeable, but the ^{78}As yield shown in Fig. 1 may bear out this suggestion. Also, it should be mentioned that the five points representing light group yields in the lower portion of this plot are strongly influencing the position at which the curve is drawn.

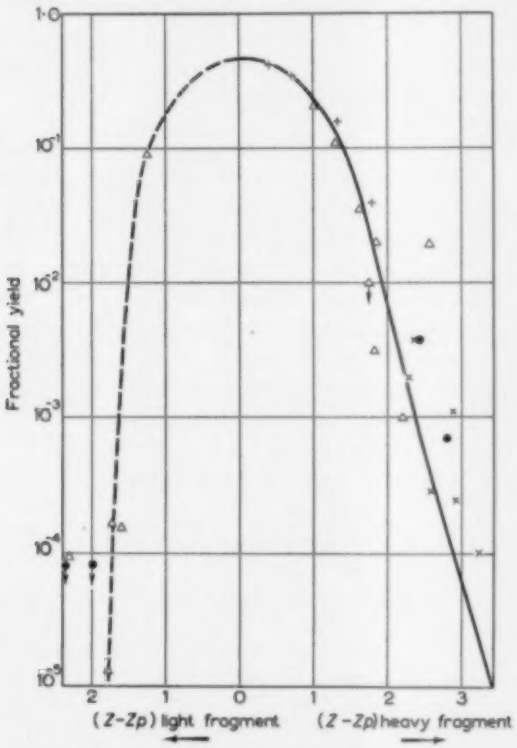


FIG. 2.—Fractional yields plotted against $(Z - Z_p)$ values derived by the maximum energy release postulate. All data given in Table 4.
△ yields taken from STEINBERG and GLENDENIN,[3]
× yields reported by KENNETT and THODE,[5]
+ yields reported by WAHL,[14]
● yields reported in this paper.
(The curves as drawn are intended simply as an aid to the inspection of the data.)

In Fig. 2 the yield data of Table 4 have been replotted according to the maximum energy release hypothesis, but keeping in mind possible asymmetries in charge distribution curves, the light and heavy fragment yields have been grouped separately. As seen from this figure the points scatter considerably. The deviations from a reasonable smooth curve are if anything a little greater than those in Fig. 1.

Since the equal chain length proposal still seems to be the most workable one, it will be used as a basis for the evaluation of the results quoted in this paper. As anticipated, the ^{140}La values appear low, being on the average about 30 per cent of that predicted by the curve (Fig. 1). If this is the result of the postulated "boil off"

of the unpaired neutron in ^{140}La, one would expect to find 70 per cent of the unperturbed ^{140}La yield at ^{139}La. Hence if the hypothesis is correct the independent yield of ^{139}La should be 20 times higher than that predicted by the curve, and although not readily observable, the corresponding data for ^{136}Xe make such a value probable. However it is apparent from the yield of ^{141}La that this neutron "boil off" effect does not extend to 3 neutrons above a shell. In the case of ^{136}Xe, which has 82 neutrons, most of the measured yield should result from prompt neutron emission fron ^{137}Xe. To obtain the data for Fig. 1, the ^{136}Xe yield predicted by the curve has been subtracted from the experimental value, and the result plotted at a $(Z - Z_p)$ for ^{137}Xe. Reasonable agreement with the predicted yield in ^{235}U is obtained in this manner, but the data for ^{233}U and ^{239}Pu are not sufficiently accurate for this treatment.

CONCLUSION

From the foregoing study it can be seen that although modification is required to account for perturbations near closed shells, the equal charge displacement hypothesis does account for the lanthanum results qualitatively, and in general still appears to be the most workable postulate. It should be pointed out, however, that there may be asymmetries in the charge distribution curves, and if such is the case a single curve probably cannot be expected to account adequately for the full range of independent yield data. However, a much larger body of accurate yield data must be accumulated before such a proposal can be considered in detail.

Acknowledgement—The authors would like to express their thanks to J. C. D. MILTON of the Physics Division, A.E.C.L., for many valuable discussions.

APPENDIX A

Radiochemical procedures

Irradiated samples were dissolved as rapidly as possible in boiling 8 N hydrochloric acid containing a drop of concentrated nitric acid to increase the rate of solution of U_3O_8. Known amounts of lanthanum, yttrium, barium and strontium carriers were added (approximately 40 mg each) and the solution was filtered to remove any undissolved particles of the irradiated material. The solution was then boiled for a further 5 min to promote exchange, diluted, mixed thoroughly, and divided into 4 aliquots. Chemical treatment of the first of these was begun immediately, while the second, third and fourth aliquots were started respectively at approximately 40 min, 1 week and 2 weeks after zero time.

The following procedure was used in each case:

(1) Three grams of hydroxylamine hydrochloride were added to complex the uranium, and the rare-earth hydroxides precipitated with gaseous ammonia. The time elapsed between this precipitation and the end of the irradiation was noted, and the time between precipitation and centrifugation was held to a minimum. By using the NRX "rabbit", and with practice and minor refinements in technique, the time required to the first precipitation was reduced to 18 min.

(2) The hydroxide was dissolved in a minimum of dilute hydrochloric acid and step 1 was repeated.

(3) The precipitate was centrifuged, redissolved, 100 mg potassium dichromate added and the solution heated to boiling for 10 min. The addition of hydrofluoric acid separated the rare earths from the bulk of the neptunium.

(4) The precipitate was dissolved in a 50–50 mixture of saturated boric and 6 N nitric acids, and the hydroxide brought down with gaseous ammonia.

(5) Ruthenium carrier was added to a hydrochloric acid solution of the precipitate and removed as ruthenium sulphide.

(6) The rare earths were recovered from the clear supernatant by repeating steps 3 and 4.

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(7) To remove any remaining contamination (except rare earths) a 9 N hydrochloric acid solution of the sample was passed through a Dowex 1A anion column, then rare-earths hydroxides were precipitated from the effluent and dissolved in concentrated hydrochloric acid. Two milligrams of cerium were added, the solution evaporated to dryness and taken up in 0·4 M lactic acid at a pH of 2·5.

(8) The sample was then adsorbed on a cation exchange column packed with 400–500 mesh Dowex 50 and maintained at a temperature of 78°C.[18] On elution with 0·4 M ammonium lactate at pH 4·1, yttrium appeared in the 20 to 40 ml fraction. This solution was followed with 0·55 M ammonium lactate at pH 5·0 which eluted cerium in the 35 to 50 ml fraction and lanthanum in the 60 to 100 ml fraction.

(9) Yttrium and lanthanum were recovered as oxalates from the respective effluent solutions by the addition of one half volume of saturated oxalic acid.

The samples were at this point removed to a low level laboratory for further purification and counting.

(10) The oxalate precipitate containing the lanthanum fraction was ignited in a platinum crucible, then dissolved in a minimum of concentrated hydrochloric acid. Two milligrams of cerium carrier were added and another column separation performed to reduce the cerium contamination a further 2000-fold. Lanthanum was recovered as the oxalate, dissolved in 3 drops of hydrochloric acid, reprecipitated from a hot 1 M solution with a half volume of saturated oxalic acid and washed twice with water, twice with absolute alcohol and once with ether, before mounting on an aluminium tray for weighing and counting. By this time all the short lived lanthanum isotopes had decayed and any deviations from a 40·2 hr half-life were taken as indications of contamination in the sample.

(11) The yttrium precipitate from steps 8 and 9 was treated somewhat differently in order to measure the amount of ^{93}Y in aliquots 1 and 2, and so check the completeness of exchange in the dissolution procedure. The oxalate was ignited, weighed and dissolved in 1 ml of dilute hydrochloric acid. Two 20 λ samples of this solution were pipetted onto stainless steel discs, ignited and counted as soon as possible. The remainder of the solution was evaporated to dryness, dissolved in 0·04 M lactic acid and another column separation undertaken to reduce the rare-earth contamination. Yttrium was recovered and mounted in a manner similar to that used for lanthanum.

APPENDIX B

Calculation of results

The following formulae have been derived for the calculation of fractional yields.

If we let Y = the total fission yield of the mass chain of which A and B are members,

N = the number of fissions per unit time,

a = the fraction of B which is formed by growth from A,

b = the fraction of B formed independently in fission,

then the differential equations governing the growth of A and B during an irradiation of time t_1 are:

$$\frac{dA}{dt} = aYN - \lambda_A A \tag{1}$$

$$\frac{dB}{dt} = aYN[1 - \exp(-\lambda_A t)] + bYN - \lambda_B B \tag{2}$$

and the number of atoms of B present at the end of the irradiation,

$$B_1 = YN\left[\frac{1}{\lambda_B} - \frac{a\exp(-\lambda_A t_1)}{\lambda_B - \lambda_A} - \left(\frac{1}{\lambda_B} - \frac{a}{\lambda_B - \lambda_A}\right)\exp(-\lambda_B t_1)\right]. \tag{3}$$

After the irradiation the growth of B,

$$\frac{dB}{dt} = \lambda_A \exp(-\lambda_A t) - \lambda_B B\ . \tag{4}$$

Integrating this expression and substituting values of A_1 and B_1 given in the preceding equations, the

[18] GWEN M. MILTON and W. E. GRUMMITT *Canad. J. Chem.* June 1957.

following expression for the number of atoms of B present at t_2 is obtained, (t_2 = time from end of irradiation to the separation of B from A):

$$B_2 = YN\left[\frac{a}{\lambda_B - \lambda_A}\left\{\exp(-\lambda_A t_2)[1 - \exp(-\lambda_A t_1)] - \exp(-\lambda_B t_2)[1 - \exp(-\lambda_B t_1)]\right\} + \frac{1}{\lambda_B}\exp(-\lambda_B t_2)[1 - \exp(-\lambda_B t_1)]\right]. \quad (5)$$

Expanding this function and collecting the first three terms:

$$\frac{B_2}{YN} \cong (1 - a)t_1 + \tfrac{1}{2}at_1(2t_2 + t_1)\left(\lambda_B + \lambda_A - \frac{\lambda_B}{a}\right) - \tfrac{1}{6}at_1\lambda_A\left[\lambda_B + \lambda_A + \frac{\lambda_B - \lambda_B^2/a}{\lambda_A}\right](t_1^2 + 3t_1t_2 + 3t_2^2). \quad (6)$$

In the case of ^{140}La this equation can be reduced to:

$$\frac{\text{Atoms of } ^{140}\text{La at } t_2}{YN} = (1 - a)t_1 + \tfrac{1}{2}at_1(2t_2 + t_1)\left(\lambda_B + \lambda_A - \frac{\lambda_B}{a}\right) - \tfrac{1}{6}at_1\lambda_A(\lambda_B + \lambda_A)(t_1^2 + 3t_1t_2 + 3t_2^2). \quad (7)$$

By a similar integration and expansion of equation (1) the number of atoms of A at t_1 can be determined to the same order of approximation,

$$\frac{A_1}{YN} \cong at_1 - \frac{a}{2}\lambda_1 t_1^2. \quad (8)$$

In the case of ^{140}Ba in the present experiments this can be reduced to

$$\frac{\text{Atoms of } ^{140}\text{Ba at } t_1}{YN} \approx at_1 \quad (9)$$

Hence

$$\frac{\text{Atoms of } ^{140}\text{La at } t_2}{\text{Atoms of } ^{140}\text{Ba at } t_1} = \frac{1 - a}{a} + \frac{(\lambda_A + \lambda_B - \lambda_B/a)}{2}(2t_2 + t_1) - \tfrac{1}{6}\lambda_A(\lambda_A + \lambda_B)(t_1^2 + 3t_1t_2 + 3t_2^2), \quad (10)$$

$$\text{and } \frac{\text{Atoms of } ^{140}\text{La at } t_2}{\text{Atoms of } ^{140}\text{Ba at } t_1} = \frac{\text{specific activity of La at time } t_2 \times \lambda_{\text{Ba}}}{\text{specific activity of Ba* at time } t_1 \times \lambda_{\text{La}}}.$$

The specific activity of lanthanum at t_2 has been measured, and the specific activity of barium at t_1 calculated by measuring the specific activity of lanthanum in samples 3 and 4 for which t_2 is very large, and substituting in the following formula:

Number of atoms of Ba at t_1 =

$$\frac{\lambda_B - \lambda_A}{\lambda_A\lambda_B} \times \text{specific activity of } ^{140}\text{La at } t_3 \times \frac{1}{\exp(-\lambda_A t_3) - \exp(-\lambda_B t_3)} \quad (11)$$

(where $t_3 = t_1$ for sample 3)

Since $1 - a = b$

$$\frac{b}{1 - b} = \frac{N_{\text{La}} \text{ at } t_2}{N_{\text{Ba}} \text{ at } t_1} - \frac{1}{2}\left(\lambda_{\text{Ba}} + \lambda_{\text{La}} - \frac{\lambda_{\text{La}}}{a}\right)(2t_2 + t_1) + \tfrac{1}{6}\lambda_{\text{Ba}}(\lambda_{\text{La}} + \lambda_{\text{Ba}})(t_1^2 + 3t_1t_2 + 3t_2^2) \quad (12)$$

These formulae were also used for the ^{91}Y calculations, however in cases where $t_2 > 0{\cdot}5$ hr it was necessary to use the exponentials rather than the approximation $e^{-x} = 1 - x$.

* Counted as ^{140}La.

J. Inorg. Nucl. Chem., 1957, Vol. 5, pp. 105 to 111. Pergamon Press Ltd., London

MEASUREMENTS ON ELECTROMAGNETICALLY SEPARATED RADIOACTIVE ISOTOPES OF IODINE

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Abstract—The mass range 124–135 of iodine isotopes formed in 170 MeV proton-induced fission of uranium has been studied using an electromagnetic isotope separator to prepare mass-determined samples for Geiger-Müller counting. Relative formation cross-sections are given for the shielded nuclides: 12·6 hr ^{130}I (1·0), 25 min ^{128}I (0·7), 13 day ^{126}I (0·4), and 4 day ^{124}I (0·1).

The presence of a (2·6 ± 0·8) hr half-life in the mass 126 decay curve may indicate isomerism in ^{126}I.

Neutron deficient iodine isotopes down to mass number 118 were separated from spallation products of caesium. The following mass assigments are reported: ^{119}I (19 min), ^{120}I (1·4 hr), and ^{121}I (2·0 hr).

THE fission of heavy elements induced by high energy particles leads to both neutron rich and neutron deficient nuclides. These are ordinarily separated, purified, and isolated by standard radiochemical methods. Quite often, however, the element of interest is present in a large number of isotopes, each with its characteristic decay. Thus the standard methods lead to samples whose direct analysis by radioactivity measurements is virtually impossible because of the large number of species present. In some of these cases, however, the difficulties can be overcome and a differentiation between the isotopes made by the use of special techniques such as daughter separation, energy selection counting, and so on. Although very valuable, these methods naturally have their limitations.

These limitations were encountered in a study of the distribution of products from fission of uranium induced by 170 MeV protons. After the determination of the mass distribution,[1] an investigation of the distribution of nuclear charge has been undertaken.[2] One of the aims of the experimental part of such a study is to measure independent (primary) fission yields. In the course of this work it was realized that measurements on the isotopes of iodine (four of them being shielded) which are present in the fission product mixture would provide valuable information for the evaluation of the charge distribution curve in the heavy fission product region. These measurements are not possible by standard methods because a chemically isolated iodine sample contains about ten radioactive isotopes with half-lives ranging from 25 min to 60 days. In the search for a technique capable of differentiating between these isotopes the possibility of using electromagnetic separation after the chemical procedure was considered.

For similar purposes mass separators have previously found only limited use.

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(1) A. KJELBERG and A. C. PAPPAS *Nucl. Phys.* **1**, 322 (1956).
(2) P. AAGAARD and A. C. PAPPAS To be published.

KOCH *et al.*[3] determined relative fission yields of some krypton isotopes, and the method was later applied by ANDERSSON[4] to solid spallation products of vanadium.

The present paper reports some measurements carried out with mass-separated iodine isotopes in the mass range 118 to 135 produced in high energy fission of uranium and in spallation of caesium, both processes induced by 170 MeV protons.

EXPERIMENTAL

Targets of uranium trioxide and caesium chloride were irradiated in the Uppsala synchrocyclotron. The target was dissolved and the iodine separated and purified according to the method described earlier.[5] After the addition of about 2 mg of carrier as iodide a specific oxidation-reduction cycle was performed in order to ensure complete exchange between the different states of the fission

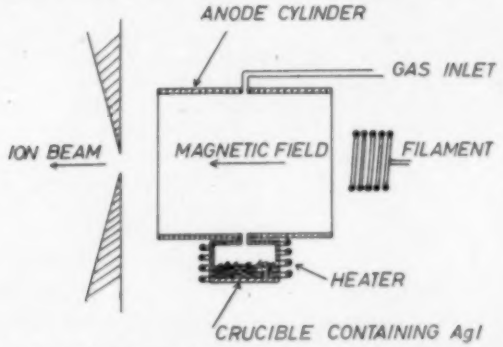

FIG. 1.—Schematic cross-section of the ion source of the mass separator.

product iodine and the added carrier. The iodine was then separated and purified by solvent extraction using selective oxidation-reduction cycles. It was finally precipitated as silver iodide. This was slurried in acetone and transferred to a crucible which fits the ion source furnace of the mass separator,[6] and the acetone was then evaporated.

As natural iodine is monoisotopic there was no experience from stable isotope separation to support the choice of silver iodide as a suitable charge material for the mass separator. In the calutrons at Oak Ridge this compound had been tried with little success in attempts to process silver.[7] As to the production of iodine ions, however, some preparatory runs with stable charge material did not reveal any appreciable difference between silver iodide and potassium iodide. Thus the former, being a convenient end product of the chemical separation, was chosen.

The small stainless steel or graphite crucible containing the silver iodide was introduced through a vacuum gate into the ion source and placed as shown in Fig. 1. In order to start the discharge argon was usually fed to the source. The supply of support gas was interrupted when the vapour pressure of iodine became high enough to sustain the discharge. Most of the silver was found to remain in the crucible.

The collection of the separated ion beams, which is a major problem in big scale isotope separation, does not offer any difficulties in this type of work. The low ion-current densities make it possible to apply the method of direct deposition owing to penetration of the ions into the collector material.[8,9] The collector arrangement used is schematically shown in Fig. 2. The distance between lines corresponding to neighbouring iodine isotopes is about 5 mm in the focal plane (at 45° to the beam direction) and the half-width of the lines was normally kept at 3 mm or less. Their height was adjusted to

[3] J. KOCH, O. KOFOED-HANSEN, P. KRISTENSEN, and W. DROST-HANSEN *Phys. Rev.* **76**, 279 (1949).
[4] G. ANDERSSON *Phil. Mag.* **45**, 621 (1954).
[5] A. C. PAPPAS *Technical Report No.* 63. Mass. Inst. of Tech., Laboratory for Nuclear Science, American Report AECU–2806 (1953).
[6] G. ANDERSSON *Ark. Fys.* In press. *cf.* J. KOCH *Proc.* 1955 *Harwell Isotope Conf.* Chapter 25.
[7] B. S. WEAVER Private communication, Sept. 1955.
[8] S. THULIN *Ark. Fys.* **9**, 107 (1955).
[9] K. O. NIELSEN *Proc.* 1955 *Harwell Isotope Conf.* Chapter 9.

25–30 mm and aluminium strips 4 mm × 40 mm with a thickness of 2·4 mg/cm² were used as collectors. The maximum penetration depth of 60 keV iodine ions into aluminium, as calculated by means of the simplified formula given by NIELSEN,[9] corresponds to 4 μg/cm².

In order to fix the position of the spectrum during operation the separator is provided with a stabilizing device, the feeler electrodes ("sniffers") of which are also indicated in Fig. 2. When large disturbances occur (e.g. sparking), causing the stabilizer to loose control, the spectrum is automatically swept away from the collector (perpendicular to the plane of the figure). In practice the sniffers were set to operate on the stable ^{127}I line.

The fairly short-lived activites involved (notably 25 min ^{128}I) made it necessary to start the mass separation as soon as possible after the chemistry was completed. Consequently it was impossible to avoid frequent electrical breakdowns and bad focusing, especially at the beginning of a separation. To minimize the resulting undesired effects, small ion currents were always used, a few μA or less for

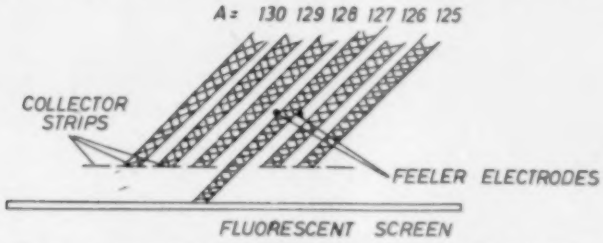

FIG. 2.—Arrangement for the collection of radioactive iodine isotopes.

mass 127. In spite of this, as much as 5 per cent of an isotope of mass number A was sometimes found on the mass A–1 collector and up to about 2 per cent on the mass A–2 collector. The ratio between the amounts of contamination on the A–2 and the A–1 collector was always constant, about 0·35. Though it was in all cases possible to correct for these contaminations in the analysis of the decay curves (thanks to large differences in half-lives of neighbouring isotopes) they no doubt constitute a source of error.

From the observed activities of the separated iodine and a simultaneously isolated fission product with known yield[1] (^{89}Sr) the overall efficiency (including the magnetic separation) for iodine in one of the runs could be estimated to be about 0·2 per cent. This is thought to be a representative figure. The activities obtained, however, were in most cases sufficient for Geiger-Müller counting. It may be added that in the above mentioned run more xenon was found on the collector foils than would correspond to the amount grown from decay of the iodine present on these foils. These data indicated an efficiency of 5–10 per cent for the mass separation of xenon.

An expected complication was the formation of IH^+ ions in the ion source, which means that part of an activity with mass A will show up as a contamination on mass number $A+1$. In the case of the noble gases, which also tend to form hydride ions, it has been found that the conditions can be improved by running the ion source for several hours before starting the separation.[10] Correspondingly a decrease in the amount of iodine hydride with increasing separation time was observed. With regard to the short-lived activities, however, the mass separations had to be performed relatively quickly, the whole procedure being completed within ½–1 hr after the chemical separation. The average hydride content was of the order of 10–15 per cent. The iodine isotopes of interest, however, show the favourable feature that neighbouring isotopes have widely different half-lives. It is then possible to correct for the contribution of the hydrides to the observed activities.

After the separation of the different isotopes the aluminium strips were removed from the collector plate and carefully mounted in the centre of the punched hole (30 mm diameter) in standard cardboard mounting cards.[5] The counting could start 1–1½ hr after the end of the irradiation and was performed according to the techniques of absolute counting described elsewhere.[5,11] As the sources are weightless and practically free from covering material the self-absorption and self-scattering are negligible.

[10] J. KOCH *Circ. Nat. Bur. Stand. No.* 522 (1953).
[11] G. RUDSTAM Inaugural Dissertation, Univ. of Uppsala (1956).

RESULTS

Isotopes of iodine from high energy fission. Fission of uranium induced by 170 MeV protons was found to produce both neutron rich and neutron deficient isotopes of iodine covering a rather broad mass region. The results of the half-life analysis of the gross decay curves observed for the samples on the different collector foils are summarized in Table 1.

TABLE 1.—ISOTOPES OF IODINE FOUND IN FISSION OF URANIUM WITH 170 MeV PROTONS

Mass number	Half-life* observed	Identification
124	3·4 ± 0·4 day	^{124}I reported 4·0 day, 4·5 day[12]
125	no short-lived activites	^{125}I reported 60·0 day[12]
126	2·6 ± 0·8 hr 13·1 ± 0·5 day	^{126}I reported 13·0 day[12]
127	stable	mass marker
128	25·4 ± 0·6 min ~13 hr	^{128}I reported 24·99 min [13] ^{130}I as contamination
129	 ~25 min ~13 hr	^{129}I reported 1·72 × 10 year[12] ^{128}I as hydride ^{130}I as contamination
130	12·5 ± 0·1 hr 8·1 day	^{130}I reported 12·6 hr[12] ^{131}I as contamination
131	8·1 ± 0·1 day ~13 hr 2·6 hr	^{131}I reported 8·0–8·1 day[12] ^{130}I as hydride ^{132}I as contamination
132	2·5 ± 0·2 hr ~8 day 20 hr ~6 day	^{132}I reported 2·26 hr[12] ^{131}I as hydride ^{132}I as contamination ^{132}Xe grown from ^{132}I in the sample
133	20 ± 2 hr 2·3 hr ~5 day	^{133}I reported 20·5 hr[12] ^{132}I as hydride ^{133}Xe grown from ^{133}I in the sample
134	54 ± 1·1 min ~21 hr ~5 day ~9 hr	^{134}I reported 52·5 min, 51 min, 54 min[12] ^{133}I as hydride ^{134}Xe grown from ^{134}I in the sample ^{134}I/^{134}Xe decay, as contamination
135	~9 hr 54 min	^{135}I/^{135}Xe decay ^{134}I as hydride

* The errors given in the measured half-lives are the standard deviations.

[12] J. M. HOLLANDER, I. PERLMAN, and G. T. SEABORG *Rev. mod. Phys.* **25**, 469 (1953).
[13] E. W. EMERY and N. VEALL *Nature, Lond.* **174**, 889 (1954).

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In the cases where the decay characteristics of the isotopes studied are known, the measured activities can be converted to absolute disintegration rates in a standard manner, using the known factors for absolute counting.[5,11] Under the assumption that the efficiency of mass separation and ion collection is the same for all isotopes of an element, yields can be computed relative to an internal monitor, e.g. ^{130}I.

In the case of shielded nuclides the computation of yields is straightforward and the results of several independent determinations are given in Table 2 for the

TABLE 2.—RELATIVE INDEPENDENT YIELDS OF IODINE ISOTOPES IN FISSION OF URANIUM WITH 170 MeV PROTONS

Mass number	Half-life	Activity observed* c/s	Independent fission yield relative to ^{130}I
124	4 day	0·8	0·09
126	13 day	1·8	0·41
128	25 min	260	0·74
130	12·6 hr	263	1·00
131	8·1 day	25·0	0·90
132	2·3 hr	1005	1·26
133	20·5 hr	194	1·45†
134	52·5 min	1230	0·88

* See text for details.
† Cumulative yield.

4 day ^{124}I, 13 day ^{126}I, and 25 min ^{128}I, all relative to 12·6 hr ^{130}I. To give a picture of the feasibility of chemical separation followed by electromagnetic separation, the activities of the various isotopes are also included in Table 2. These were typical of standard runs under the following conditions:

About 1 hr of irradiation of 0·75 g uranium trioxide in a proton beam intensity of 1 μA, ~15 min of decay before chemical separation of iodine from the gross fission mixture (chem. yield 60 per cent) followed by the electromagnetic separation, resulting in a 1½ hr total decay before counting of the collector foils.

The large variation in the activities (given in Table 2) from one isotope to another is the result of the difference in half-lives and fission yields of the isotopes of interest.

The determination of cumulative fission yields[1,2] has disclosed that the mass distribution curve for fission of uranium induced by 170 MeV protons is nearly flat in the mass region where the isotopes of iodine occur. This permits an intercomparison of the shielded isotopes of iodine, as shown in Fig. 3, where the logarithm to the relative independent yields is plotted as a function of the mass number. On the basis of fission systematics[5] one expects a smooth bell-shaped curve for the mass-dependence of the fractional independent yield of the isotopes of a given element. The curve in Fig. 3 is consistent with this.

Having the curve in hand one is able to apply the small correction necessary to account for the contribution of the decay of precursors to the measured activities

of the non-shielded isotopes of iodine: 8·1 day ^{131}I, ^{132} 2·3 hr I, and 52·5 min ^{134}I with parents 30 hr/25 min ^{131m}Te/^{131g}Te, 77·7 hr ^{132}Te, and 44 min ^{134}Te, respectively.

The independent fission yields for these isotopes (relative to the yield of 12·6 hr ^{130}I) obtained in this way are given in the last column of Table 2.

A more detailed discussion of these results and their bearing on the high energy fission process will appear, together with data on other fission products, in a separate communication.[2]

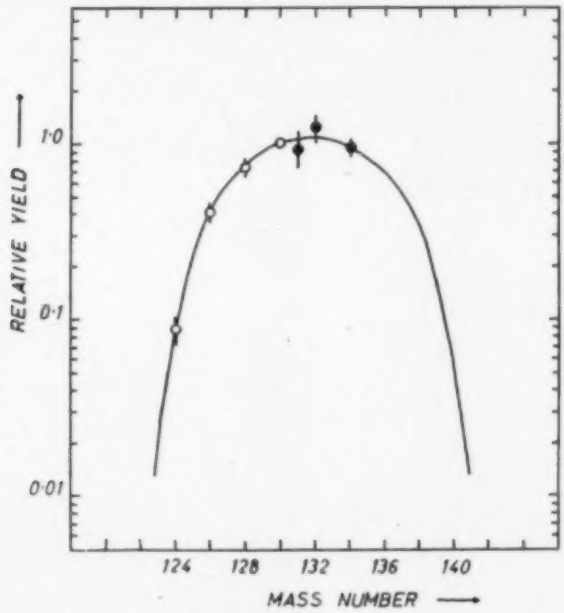

FIG. 3.—Distribution of independent yields of iodine isotopes with mass.
○ Shielded isotopes
● Non-shielded isotopes

Possible isomerism in ^{126}I. All contaminating components in the decay curves of the various mass numbers could, as Table 1 discloses, be accounted for by the effects mentioned in the experimental section, with one prominent exception, namely that of a (2·6 ± 0·8) hr activity at mass 126. It was present in all the runs as a constant fraction of the 13 day activity known to be due to the ^{126}I ground state.[12] One possible explanation is clearly isomerism in ^{126}I which would not be contradictory to shell theory expectations. From systematics of the independent yields of isotopes of iodine[2] the suggested isomeric state of ^{126}I should not show any appreciable decay by *K*-capture or β-emission. This interpretation receives some indirect support from work at Berkeley on Sb(α,*xn*) reactions where an anomalously low yield of 13 day ^{126}I was obtained by a fast separation of iodine.[14]

The intensity of the 2·6 hr activity obtained from uranium fission was too weak to allow any detailed investigation of its decay characteristics. Attempts to make stronger samples by Te(*p*,*xn*) reactions and by spallation of caesium and then to confirm an assumed internal transition relationship between the two activities

[14] I. PERLMAN Private communication. Nov. 1955.

concerned by studying the growth and decay of the 380 keV γ-ray following ^{126}I in a scintillation spectrometer also failed. There was, however, always an indication of the shorter half-life in the mass 126 disintegration curves. Pending improved techniques of sample preparation the question of isomerism in ^{126}I cannot be settled.

Isotopes of iodine from spallation of caesium. Spallation of caesium induced by 170 MeV protons was found to produce highly neutron deficient iodine isotopes in quite good yields. In order to check some previously uncertain mass assignments the decay curves of mass numbers 118–122 were measured. The main results are summarized in Table 3.

TABLE 3.—ISOTOPES OF IODINE FOUND IN SPALLATION OF CAESIUM WITH 170 MeV PROTONS

Mass number	Half-life observed	Identification
118	2·0 hr ≈10 min	Possibly ^{117}Te as hydride; 2·5 hr $<^{118}$Te reported earlier[12]
119	2·2 hr 19 min	Hydride of 2 hr activity on 118 excluded for intensity reasons. ^{119}I reported 18 min[15] and 17 min[16]
120	1·4 hr	^{120}I reported $\geq$ 1·1 hr[16] and $>$ 1·3 hr[17]
121	2·0 hr	^{121}I reported 1·5 hr and 1·8 hr,[13] 1·6 hr[17]
122	2·0 hr	^{121}I as hydride

As the measurements were of a preliminary nature, a closer study of these activities will be undertaken in connection with a future investigation of the corresponding xenon isotopes.

Acknowledgements—The authors wish to express their thanks to Prof. T. SVEDBERG, director of the Gustaf Werner Institute for Nuclear Chemistry, for his interest in this work and to CERN, Theoretical Study Division, for providing fellowships which enabled two of us (P. Aa. and A. C. P.) to perform this study. We also wish to thank the staff of the Uppsala synchrocyclotron for help during the bombardments.

[15] G. B. ROSSI, W. B. JONES, J. M. HOLLANDER, and J. G. HAMILTON *Phys. Rev.* **93**, 256 (1954).
[16] B. DROPESKY Thesis, Univ. of Rochester (1953).
[17] R. W. FINK Thesis, Univ. of Rochester (1953).

J. Inorg. Nucl. Chem., 1957, Vol. 5, pp. 112 to 117. Pergamon Press Ltd., London

MOLECULAR DISSOCIATION FOLLOWING RADIOACTIVE DECAY: TRITIUM HYDRIDE

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(*Received* 4 *April* 1957)

Abstract—When radioactive decay takes place in the TH molecule, the resulting $(He^3H)^+$ ion shows a strong tendency to remain bound. When dissociation does take place, the electrons most commonly divide one with each nucleus, rather than both going either with the He^3 fragment or with the H fragment. These conclusions are derived from a magnetic analysis of the ions produced as the result of TH decay, the observed relative intensities being as follows: $(He^3H)^+$, 93·2 ± 1·9 per cent; $(He^3)^+$, 5·1 ± 0·3 per cent; H^+, 1·55 ± 0·16 per cent; $(He^3)^{++}$, 0·14 ± 0·01 per cent. The molecule loses an electron in fewer than 1·7 per cent of the decay events.

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AFTER the tritium atom in a TH molecule undergoes radioactive decay, the $(He^3H)^+$ molecular ion that is immediately produced will in general be in a state of considerable excitation. The reasons for the excitation are evident; the transformation of T to He^3 can produce excitation of the electrons because of the change in their electrostatic environment, and it can similarly induce vibration because of the change in the coulomb force between the nuclei. In addition, the nuclear recoil from the beta-neutrino emission (amounting in the case of a free T atom to a maximum value of 3·3 eV and having a most frequent value only slightly smaller) will produce vibration and rotation, not to mention translatory motion that need not concern us here. As a result, there will be an expectation that in some of the decay events the molecular ion may dissociate, and that in doing so it may or may not lose one of its electrons.† On the other hand, $(HeH)^+$ is known to be stable; it has been observed in mass spectrometry,[1–3] and several computations[4–8] have been made of its binding energy, the most recent of these leading to values slightly under 2 eV. Accordingly, there exists also an expectation that some of the $(He^3H)^+$ ions may remain bound.

Theoretical treatments of the radioactive dissociation problem have recently been given by SCHWARTZ[9] and by CANTWELL,[10] who have applied to molecules a quantum-mechanical "sudden perturbation" calculation analogous to the calculations that have been applied rather successfully to atoms in accounting for the ionization

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† The possibility of double electron loss we dismiss as remote, and by implication the results of the experiment to be described in this paper strongly support that expectation. $(HeH)^{++}$ is expected to be unstable (refs. 4, 5).

[1] F. W. ASTON *Isotopes* p. 129. Edward Arnold, London (1924).
[2] T. R. HOGNESS and E. G. LUNN *Phys. Rev.* **26**, 44 (1925).
[3] K. T. BAINBRIDGE *Phys. Rev.* **44**, 57 (1933).
[4] J. Y. BEACH *J. chem. Phys.* **4**, 353 (1936).
[5] C. A. COULSON and W. E. DUNCANSON *Proc. roy. Soc.* A **165**, 90 (1938).
[6] S. TOH *Proc. phys.-math. Soc. Japan* **22**, 119 (1940).
[7] A. A. EVETT *J. chem. Phys.* **24**, 150 (1956).
[8] A. C. HURLEY *Proc. phys. Soc.* A **69**, 868 (1956).
[9] H. M. SCHWARTZ *J. chem. Phys.* **23**, 400 (1955).
[10] M. CANTWELL *Phys. Rev.* **101**, 1747 (1956).

that results from the abrupt change in nuclear charge accompanying beta decay.[11] We shall see, however, that only a rather limited comparison can be made between the predictions of theory in their present form and the results of the experiment now to be described.

EXPERIMENTAL

The apparatus used for these measurements has been described elsewhere in its application to the charge spectrometry of radioactive rare gases,[12] but a brief recapitulation may be appropriate here. The gas under investigation is made to flow through a vessel called a "source volume" at a total pressure of 4×10^{-6} mm Hg (in the case of TH), and inside the source volume there is a conical array of ring-shaped electrodes producing an electric field whose lines of force converge toward an opening, half an inch in diameter, at the small end. The electrode assembly encloses a volume of about $\frac{1}{2}$ l., and positive ions formed therein are accelerated and roughly focused toward the opening. The opening is at the object position of a magnetic analyser that deflects the charged particles through 96·5 deg. and re-focuses them bi-directionally toward an image position where they are counted by means of an electron multiplier. The ring electrodes are biased positively by 1 to 5 kV with respect to the magnetic analyser at ground potential, with an additional 80 to 400 V distributed from one end of the electrode assembly to the other. Sweeping over a peak in detail shows that the distribution of this collecting voltage is such that the exact point of origin within the source volume is of minor importance in determining the total energy of ions entering the analyser, and a single setting of the analyser suffices for the intensity determination of an ion peak with a given e/m value. When ions of differing charge values are to be compared in number, the accelerating and focusing voltages are adjusted so as to be inversely proportional to the charge under consideration, thereby ensuring an efficiency of collection and focusing that is uniform from charge to charge. After the magnetic deflection, the ions undergo an additional acceleration toward the first dynode of the multiplier at −5 kV with respect to ground, and this gives them a comfortable energy for counting. Strong differential pumping is applied across both the object and image positions of the analyser to keep the radioactive gas away from the detector. When corrections have to be applied to compensate for changes in detector efficiency from one kind of ion to another, they are evaluated by means of integral bias curves; the corrections usually amount to less than 10 per cent. In summary, the apparatus in this application can be described as an adaptation of the mass spectrometer to the use of low-pressure radioactive gas as an ion source.

It is usually convenient to use a beta-gamma counter to monitor the radioactive strength of the gas in the source volume, but in this case the counter was ineffective because of the low energy of the tritium beta rays. Accordingly, source depletion curves were taken during the various series of measurements by following the intensity of the mass 4 peak as a function of time, and the effective source strengths for other peaks were then derived by interpolation. Counting rates were high, ranging from 119 counts/min for $(He^3)^{++}$ to 45,000 counts/min for $(He^3H)^+$.

It is useful to choose TH rather than T_2 for investigation in order that the two

[11] J. S. Levinger *Phys. Rev.* **90**, 11 (1953); H. M. Schwartz *J. chem. Phys.* **21**, 45 (1953); P. Benoist-Gueuthal *Ann. Phys.* **8**, 593 (1953).
[12] F. Pleasonton and A. H. Snell *Proc. roy. Soc.* A, in course of publication.

halves of a dissociated molecule can be separately recognized. A hydrogen mixture containing about 50 per cent of tritium was chosen for examination, and since it had aged by more than a month since preparation, the equilibrium constant of DORFMAN and MATTRAW[13] was assumed to hold; viz. $(HT)^2/(H_2)(T_2) = 2{\cdot}85 \pm 0{\cdot}06$. We shall see shortly how this information can be used with the observed mass 4 and mass 6 counting rates in the analysis of the experimental data.

RESULTS

The observed relative intensities of the various ions are given in the third column of Table 1, with our estimates of the 50 per cent probable error that take into account inaccuracies in the application of corrections for multiplier efficiency and for source

TABLE 1.—RELATIVE INTENSITIES OF IONS PRODUCED IN THE RADIOACTIVITY OF A MIXTURE OF H_2, TH, AND T_2

e/m	Ion identification	Relative intensity measured (decay ionization + impact ionization) per cent	Relative intensity derived (decay ionization alone) per cent (renormalized)
1	H^+	$0{\cdot}68 \pm 0{\cdot}07$	$0{\cdot}68 \pm 0{\cdot}07$
1/2	H_2^+	$0{\cdot}23 \pm 0{\cdot}01$	—
1/3	T^+, $(He^3)^+$ unresolved	$5{\cdot}9 \pm 0{\cdot}3$	$5{\cdot}9 \pm 0{\cdot}3$
2/3	$(He^3)^{++}$	$0{\cdot}14 \pm 0{\cdot}01$	$0{\cdot}14 \pm 0{\cdot}01$
1/4	$(He^3H)^+$, $(TH)^+$ unresolved	$40{\cdot}8 \pm 0{\cdot}8$	$40{\cdot}9 \pm 0{\cdot}8$
1/6	$(He^3T)^+$, T_2^+ unresolved	$52{\cdot}2 \pm 1{\cdot}8$	$52{\cdot}4 \pm 1{\cdot}8$

depletion. Neutral atoms are of course not observed, but since every decay leads to at least one charged particle, all events are represented. A strong probability that the molecular ion remain bound is immediately apparent from the data.

We recognize that the presence of H_2^+ indicates a small amount of impact ionization of the gas by the beta particles. This must also be contributing slightly to the $e/m = 1/4$ and the $e/m = 1/6$ peaks, as suggested by the alternate ion identifications given in the second column. The associated corrections can be evaluated with sufficient accuracy by taking the figures 40·8 and 52·2/2 as representing the relative concentrations of TH and T_2 respectively (the factor 2 arising from the fact that T_2 is twice as likely to undergo decay during an experimental time-interval as is TH), together with the equilibrium constant of the mixture mentioned earlier, to solve for the molecular-isotopic constitution of the gas.* Assuming equal cross-sections for impact ionization of H_2, TH, and T_2, the observed intensity of H_2^+ can then be weighted according to the molecular-isotopic constitution to yield the contributions to the mass 4 and 6 peaks that arise from impact ionization. After application of these

* This is H_2, 25 per cent; TH, 46 per cent; T_2, 29 per cent. The figures are, however, not used sensitively in the analysis of the data.

[13] L. M. DORFMAN and H. C. MATTRAW *J. phys. Chem.* **57**, 723 (1953). A discrepancy with the result of S. O. THOMPSON and O. A. SCHAEFFER *J. chem. Phys.* **23**, 759 (1955) is not large enough to affect our results.

corrections and renormalization to 100 per cent, the figures of column 4 are derived, as applying to decay ionization alone.

We next recognize three sources for the singly-charged ions of mass 3: there is T^+, which can originate only from T_2 decay, $(He^3)^+$ also from T_2 decay, and $(He^3)^+$ from TH decay. For simplicity we shall direct our attention to the evaluation of the last. Let the symbols $[T]^+$, $[He^3]^+_{TT}$, and $[He^3]^+_{TH}$ represent the intensity contributions from these three sources respectively. Then we have from Table 1, column 4,

$$[T]^+ + [He^3]^+_{TT} + [He^3]^+_{TH} = 5{\cdot}9. \tag{1}$$

We now assume that TH and TT dissociate equivalently; that is, we neglect the differences between their vibrational states in so far as the latter may affect the dissociation probabilities. Under this assumption

$$[T]^+ = [H]^+ [He^3T]^+/[He^3H]^+ = 0{\cdot}68\ (52{\cdot}4/40{\cdot}9) \tag{2}$$

and

$$[He^3]^+_{TT} = [He^3]^+_{TH}\ (52{\cdot}4/40{\cdot}9). \tag{3}$$

Solution of the three equations gives, in particular, $[He^3]^+_{TH} = 2{\cdot}2$.
Likewise, for the doubly-charged ions we have

$$[He^3]^{++}_{TH} + [He^3]^{++}_{TT} = 0{\cdot}14 \tag{4}$$

and

$$[He^3]^{++}_{TT} = [He^3]^{++}_{TH}\ (52{\cdot}4/40{\cdot}9), \tag{5}$$

the solution of which gives, in particular, $[He^3]^{++}_{TH} = 0{\cdot}061$.

We can now collect the information that is pertinent to TH and renormalize to 100 per cent, thereby arriving at the figures of Table 2, which represent the result of the experiment.

DISCUSSION

The preference noted earlier of the molecular ion to remain bound finds its quantitative expression in Table 2. The figures also can be used to set an upper limit to the probability of electron loss, because that process must lead to $(He^3)^{++}$ or to H^+, and the sum of the probabilities of those fragments is 1·7 per cent. If there is dissociation without electron loss, the two electrons prefer to go one with each fragment—an observation that would not be expected on the basis of atomic ionization potentials, because it requires 11·0 eV more in energy than the break-up into neutral He^3 and charged hydrogen. On the other hand, it appears that since the energy of excitation has its source in the nuclear disintegration energy of T (18 keV), there is so much available that the 11·0 eV difference in the energies for the two modes of dissociation is not a controlling factor.

The experimentally observed preference of the two electrons to go one with each fragment rather than dissociate into a He atom and a proton may be related to a preponderance in the excited state of $(He^3H)^+$ of covalent states as compared with ionic states. It might be interesting to point out that according to both BEACH[4] and COULSON and DUNCANSON[5] in the ground state (at the equilibrium distance) of (He^+H), qualitatively two-thirds of the stability may be assigned to the formation of a covalent bond and only one-third to the formation of an ionic bond (e.g. polarization of the He atom by the proton).

We did not look for the H^- ions because we would have been led to an awkward situation with regard to the potentials applied to the electron multiplier; evidently, however, the experiment could in principle be thus extended to a differentiation between the two possible modes of formation of the $(He^3)^{++}$. This would lead to only a small further restriction to the upper limit on the probability of electron loss, because most of the latitude within the limit originates in the observed abundance of H^+.

The numbers in the second column of Table 2 are interpretable quite accurately as relative probabilities for the various modes of decay, the only possibility of

TABLE 2.—RELATIVE PROBABILITIES OF OCCURRENCE OF VARIOUS IONS FOLLOWING BETA DECAY IN TH

Ion	Probability of occurrence (per cent)	Inferred mode of dissociation (a) with no electron loss (b) with electron loss
$(He^3H)^+$	$93{\cdot}2 \pm 1{\cdot}9$	remains bound
$(He^3)^+$	$5{\cdot}1 \pm 0{\cdot}3$	(a) $(He^3)^+ + H^\circ$ (b) $(He^3)^+ + H^+$
H^+	$1{\cdot}55 \pm 0{\cdot}16$	(a) $(He^3)^\circ + H^+$ (b) $(He^3)^+ + H^+$
$(He^3)^{++}$	$0{\cdot}14 \pm 0{\cdot}01$	(a) $(He^3)^{++} + H^-$ (b) $(He^3)^{++} + H^\circ$

ambiguity being that the decays may have been over-counted because some of them may have yielded more than one charged particle. Again, the upper limit to the uncertainty in this identification is given by the sum of the H^+ and $(He^3)^{++}$ intensities, viz. 1·7 per cent.

The comparison of the experimental results with the calculations of CANTWELL and of SCHWARTZ leads to no conflict, although it is far from a critical comparison. The theoretical results give a figure for the probability of electronic ground-state to ground-state transitions between TH and $(He^3H)^+$. Using the H_2 wave functions of JAMES and COOLIDGE,[15] and the $(HeH)^+$ wave functions of TOH,[6] SCHWARTZ arrives at a value of 93 per cent for this probability, although he has since found that the wave functions of EVETT[7] for $(HeH)^+$ lead to a value of 71 per cent.[16] CANTWELL also uses the JAMES and COOLIDGE functions for H_2, but finds that a refinement in the $(He^3H)^+$ wave function can cause a decrease in the probability from 72 per cent to 58 per cent. In conjunction with these figures, our results showing that the electrons are excited to ionization in fewer than 1·7 per cent of the decays imply that many of the molecular ions are electronically excited and that therefore $(HeH)^+$ can remain bound despite some degree of electronic excitation.

While the figures in Table 2 undoubtedly give the main features of the dissociation following TH decay, nevertheless it is unfortunate that within the limitations of the analysis that had to be applied to the primary observations, any vibrational sensitivity

[15] H. M. JAMES and A. S. COOLIDGE *J. chem. Phys.* **1**, 825 (1933).
[16] H. M. SCHWARTZ Private communication (1956).

of the dissociation probabilities in $(He^3H)^+$ as compared with $(He^3T)^+$ had to be ignored. In this framework, the conclusions of Table 2 actually apply equivalently to TH and to T_2. Nevertheless, differences would be expected to exist, although they may be minor inasmuch as both $(He^3H)^+$ and $(He^3T)^+$ clearly remain predominantly bound. To reveal a sensitivity to the different vibrational states, one should use gas mixtures more dilute in tritium than 50 per cent, for then the T_2 molecules would be uncommon, and the great majority of the mass 3 fragments could be identified with TH decay. Unfortunately, this experimental refinement could not be applied in the present work, because the contamination of the apparatus quickly became so severe that it put a stop to the measurements. Therefore an extension of the experiment to tritium-dilute TH, tritium-dilute TD, and perhaps also to T_2 has much appeal, and it may soon be attempted by one of us (H. E. L.).

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THE THERMAL DECOMPOSITION OF YTTRIUM, SCANDIUM, AND SOME RARE-EARTH CHLORIDE HYDRATES

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Abstract—The thermal decomposition of yttrium, scandium, lanthanum, cerium, praseodymium, neodymium, samarium and gadolinium chloride hydrates was studied on the thermobalance. The salts began to lose water of hydration in the 55 to 110°C temperature range. Horizontal weight levels were found in the decomposition curves which corresponded to the 1-hydrate, metal oxychloride, and in some cases the metal oxide. The thermal decomposition product, in all cases except scandium and cerium, was the metal oxychloride. The minimum temperature limits for the metal oxychlorides ranged from 445 to 680°C.

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WHEN the rare-earth chloride hydrates are heated in air to moderately high temperatures, the rare-earth oxychlorides (MOCl) are formed.[1]

The temperatures at which the oxychlorides are formed are in most cases not clearly defined. BAXTER and STEWART[2] found that an oxychloride of indefinite composition was obtained when $PrCl_3 \cdot 7H_2O$ was heated in air to 115°C. Upon heating $NdCl_3 \cdot 6H_2O$ in air or steam, MATIGNON[3] found that NdOCl was obtained, which did not fuse at 1000°C.

A comprehensive study of the preparation and properties of the cerium group oxychlorides was made by MAZZA, IANDELLI, and BOTTI.[4] They found that upon heating the rare-earth chloride hydrates in air, a mixture of basic compounds of variable composition, containing rare-earth oxide, chloride, and oxychloride, was obtained. To prepare the pure metal oxychloride, it was necessary to heat the hydrated chloride to the highest temperature at which the oxychloride was stable. This temperature, for NdOCl, was stated to be 400 to 500°C. The relative thermal stability of the rare-earth oxychlorides was also determined; the thermal stability, arranged in order of decreasing stability was:

$$La \geqslant Nd > Sm > Pr.$$

More recently, studies have been conducted on the thermodynamic properties of the actinide and rare-earth oxychlorides.[5] The vapour phase hydrolysis of lanthanum, praseodymium, samarium, and gadolinium chloride has been studied in the temperature range of 700 to 900°K.[6,7,8]

[1] J. W. MELLOR *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. V. Chapter XXXVIII. Longmans, Green, London.
[2] G. P. BAXTER and O. J. STEWART *J. Amer. chem. Soc.* **37**, 516 (1915).
[3] C. A. MATIGNON *Ann. Chim. (Phys.)* (8) **8**, 243 (1906).
[4] L. MAZZA, A. IANDELLI, and E. BOTTI *Gazz. chim. ital.* **70**, 57 (1940).
[5] C. W. KOCH *United States Atomic Energy Commission, UCRL–2286* (1953).
[6] C. W. KOCH, A. BROIDO, and B. B. CUNNINGHAM, *J. Amer. chem. Soc.* **74**, 2349 (1952).
[7] C. W. KOCH and B. B. CUNNINGHAM *Ibid.* **75**, 796 (1953).
[8] C. W. KOCH and B. B. CUNNINGHAM *Ibid.* **76**, 1471 (1954).

The purpose of this study was to investigate the thermal decomposition of the scandium, yttrium, and rare-earth chloride hydrates on the thermobalance. By means of this technique it is possible to determine the presence of any intermediate decomposition products that are formed, as well as to establish their thermal stability ranges.[9] The thermal stability temperatures are not equilibrium values because of the heating rate employed. They are reproducible, however, and give some indication as to the relative thermal stability of the intermediate and final decomposition products.

EXPERIMENTAL

Thermobalance. An automatic recording thermobalance was used. The sample sizes weighed from 90 to 100 mg. The heating rate on all the samples was 5·4°C per min. A slow stream of air was passed through the furnace during the decomposition.

Chemicals. The rare-earth compounds, except that of cerium, were obtained in the form of the oxides of 99·9 per cent purity from Research Chemicals, Inc., Burbank, Calif. The cerium was obtained as $CeCl_3 \cdot 6H_2O$ from the Lindsay Chemical Co., West Chicago, Ill. Scandium oxide of 99·8 per cent purity was obtained from A. D. Mackay, Inc., New York, N.Y.

Preparation of the rare-earth chloride hydrates. The rare-earth oxides were dissolved in a minimum volume of 5N HCl, evaporated to a small volume, and allowed to crystallize in a desiccator over concentrated H_2SO_4. The resulting crystals were ground to a powder and decomposed on the thermobalance.

DISCUSSION

The thermal decomposition curves of the scandium, yttrium, and rare-earth chloride hydrates are given in Figs. 1 and 2. The composition data are given in Table 1.

TABLE 1.—THE THERMAL DECOMPOSITION OF THE RARE-EARTH CHLORIDE HYDRATES; WEIGHT LOSS DATA

Hydrate	Weight loss (per cent)							
	$MCl_3 \cdot H_2O$		MCl_3		MOCl		Other	
	found	calc.	found	calc.	found	calc.	found	calc.
$LaCl_3 \cdot 7H_2O$			34·6	34·06	49·5	49·74		
			34·7		49·4			
							CeO_2	
$CeCl_3 \cdot 6H_2O$			35·8	31·47			52·6	52·44
			34·0				52·8	
$PrCl_3 \cdot 7H_2O$			34·7	33·67	47·9	48·48		
			34·5		47·9			
$NdCl_3 \cdot 6H_2O$	26·3	25·12	31·4	30·12	45·7	45·44		
	25·8		31·6		45·3			
$SmCl_3 \cdot 6H_2O$	26·3	24·69	32·2	29·62	44·8	44·67		
	26·2		32·2		44·6			
$GdCl_3 \cdot 6H_2O$	27·1	24·26	33·2	29·11	34·9	43·89		
	27·2		33·1		43·8			
$YCl_3 \cdot 6H_2O$					53·7	53·73		
					53·7			
$ScCl_3 \cdot 6H_2O$							Sc_2O_3	
							71·8	73·38
							71·6	

[9] C. DUVAL *Inorganic Thermogravimetric Analysis* Elsevier, Houston (1953).

Lanthanum. The hydrate, $LaCl_3 \cdot 7H_2O$, began to lose water of hydration at 85°C. From 210 to 375°C a horizontal weight level was obtained which had a composition corresponding approximately to the anhydrous salt, $LaCl_3$. Since the weight loss found was greater than the calculated value, it is probable that it contained some LaOCl as a contaminant. At 375°C this mixture began to hydrolyse to give the LaOCl level, beginning at 680°C. Although not indicated in Fig. 1, there was no decomposition of LaOCl up to 850°C.

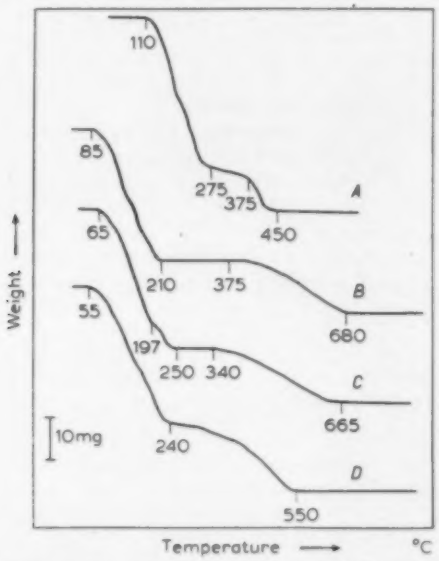

FIG. 1.—Thermal decomposition curves of the hydrates.
A. $YCl_3 \cdot 6H_2O$.
B. $LaCl_3 \cdot 7H_2O$.
C. $PrCl_3 \cdot 7H_2O$.
D. $CeCl_3 \cdot 6H_2O$.

Cerium. The thermal decomposition of $CeCl_3 \cdot 6H_2O$ was interesting in that CeO_2 was the end product instead of CeOCl. This behaviour was similar to the thermal decomposition of $Ce(NO_3)_2 \cdot 6H_2O$; in this case no $CeOnO_3$ was found.[10]

The hydrated salt began to lose water at 55°C. At 240°C a break in the curve, but not a horizontal weight level, was observed which (at 240°C) corresponded to $CeCl_3$ contaminated with either CeO_2 or CeOCl. A gradual decomposition then ensued to give CeO_2, beginning at 550°C. A horizontal weight level which corresponded to CeOCl was not found.

Praseodymium. The hydrate, $PrCl_3 \cdot 7H_2O$, had a slightly different thermal decomposition curve in that a break was observed which corresponded approximately to the 1-hydrate, $PrCl_3 \cdot H_2O$. This type of curve is also to be found with the hydrated chlorides of neodymium, samarium, and gadolinium.

The hydrate began to lose water at 65°C. A break in the curve was observed at 197°C which corresponded approximately to the 1-hydrate. From 250 to 340°C a horizontal weight level was found which corresponded to anhydrous $PrCl_3$, which was

[10] W. W. WENDLANDT *Analyt. chim. Acta* **15**, 435 (1956).

probably contaminated with PrOCl. This mixture gradually hydrolysed to give the PrOCl level beginning at 665°C.

Neodymium. The hydrate, $NdCl_3 \cdot 6H_2O$, began to lose water at 80°C. At 185°C a break was observed which corresponded approximately to the 1-hydrate, $NdCl_3 \cdot H_2O$. Actually, a horizontal weight level was found over a range of about 15°C, but this does not show up on the curve in Fig. 2. The 1-hydrate decomposed to give

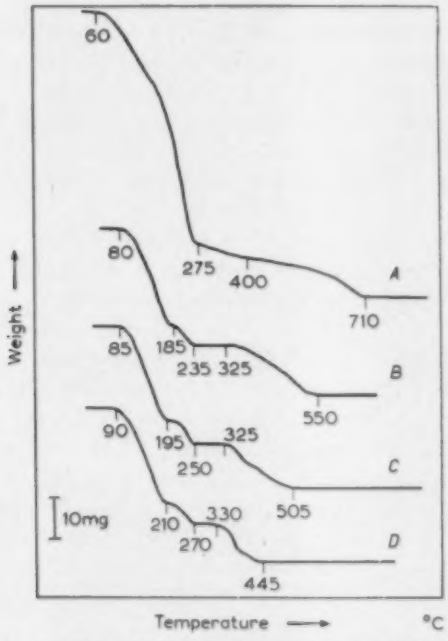

FIG. 2.—Thermal decomposition curves of the hydrates.
A. $ScCl_3 \cdot 6H_2O$.
B. $NdCl_3 \cdot 6H_2O$.
C. $SmCl_3 \cdot 6H_2O$.
D. $GdCl_3 \cdot 6H_2O$.

a horizontal weight level from 250 to 325°C which corresponded to the anhydrous salt, $NdCl_3$, contaminated with NdOCl. The NdOCl level began at 550°C.

Samarium. The hydrate, $SmCl_3 \cdot 6H_2O$, began to lose water at 85°C. A short horizontal weight level was observed at 195°C which corresponded approximately to the 1-hydrate, $SmCl_3 \cdot H_2O$. The 1-hydrate decomposed to give a horizontal weight level from 250 to 325°C. This level corresponded to the anhydrous salt $SmCl_3$, contaminated with SmOCl. At 505°C the horizontal weight level corresponding to SmOCl began.

Gadolinium. The hydrate, $GdCl_3 \cdot 6H_2O$, began to lose water at 90°C. At 210°C a break in the curve was found which corresponded approximately to the 1-hydrate, $GdCl_3 \cdot H_2O$. After further decomposition, a horizontal weight level was found from 270 to 330°C which corresponded to the anhydrous salt, $GdCl_3$, contaminated with GdOCl. The horizontal weight level corresponding to GdOCl began at 445°C.

Yttrium. The hydrate, $YCl_3 \cdot 6H_2O$, began to lose water at 110°C. This

hydrate was the most stable of all of the compounds studied. A break in the curve was observed at 275°C but, unlike the rare-earth hydrates, a horizontal weight level was not obtained. Beyond 375°C the decomposition was quite rapid to give the YOCl level beginning at 450°C.

Scandium. The thermal decomposition of $ScCl_3 \cdot 6H_2O$ was similar to $CeCl_3 \cdot 6H_2O$ in that an oxychloride was not found. However, some ScOCl was formed, inasmuch as the residue, after dissolution in 6N HNO_3, gave a chloride test with $AgNO_3$.

The hydrate began to lose water at 60°C. The decomposition was rapid all the way to 275°, where a break in the curve was found. Beyond this point the decomposition was slower, eventually giving the oxide, Sc_2O_3, at 710°C. A horizontal weight level was not found for the anhydrous salt, $ScCl_3$, or the oxychloride, ScOCl.

General observations. The thermal decomposition curves of the hydrated chlorides of La, Pr, Nd, Sm, and Gd were all similar in appearance. It can readily be seen that the ease of oxychloride formation is related to the decreasing basicity of the metal ion. The composition data for the assumed anhydrous metal chloride levels deviate more from the theoretical weight-loss values as the basicity of the metal ions decrease. For the $LaCl_3$ level the difference was about 1·7 per cent, while the $GdCl_3$ level difference was 14·1 per cent. This deviation is caused by an increasingly greater content of metal oxychloride. With the even less basic yttrium, a horizontal weight level was not observed for YCl_3, due to the increased tendency to form YOCl.

The minimum metal oxychloride temperatures also decrease with the decrease in basicity of the metal ions. For lanthanum the LaOCl level began at 680°C while for gadolinium the GdOCl level began at a much lower temperature, 445°C.

Scandium and cerium decomposed differently in that the terminal product was the oxide, and not the oxychloride.

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DIE ROLLE DER SÄURENKONZENTRATION BEI OXYDATIONEN MITTELS CHROMATS

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Abstract—The authors studied the reduction of chromic acid by means of some organic substances and confirmed that the velocity of the reaction is due to the formation of chromium (IV) in those cases, when in the reaction two electrons take part. The formation of chromium (IV) is influenced by the concentration of sulphuric acid. This phenomenon can be explained by the formation of *iso*polychromic acids.

DAS Bichromat* wird in vielen Fällen sowohl in der analytischen als auch in der präparativen Chemie als energisches Oxydationsmittel angewandt. Wir wollen uns bloss mit einem kleinen Teil dieses ausgedehnten Gebietes befassen und die Chromatoxydation einiger organischer Stoffe behandeln.

Vor kurzem wandten wir das Chromat zur Lösung konkreter analytischer Aufgaben[1–2] bei der Bestimmung von Methyl-bzw. Äthylalkohol an. SCHULEK und RÓZSA[3] gebrauchten zur Oxydation des Äthylalkohols eine Chromatlösung in 73%-iger Schwefelsäure. Unter solchen Umständen wird der Äthylalkohol zu Essigsäure, der Methylalkohol zu Kohlendioxyd oxydiert. SCHULEK und RÓZSA fanden die optimale 73%-ige Schwefelsäurekonzentration nicht auf Grund theoretischer Überlegungen, sondern nach langer experimenteller Arbeit auf empirische Weise.

Wir stellten im Rahmen unserer Untersuchungen fest, dass im Einklang mit den Angaben von SCHULEK und RÓZSA die Oxydation der oben erwähnten beiden Alkohole in 73%-iger Schwefelsäure mittels Chromats sehr rasch, dh. praktisch augenblicklich erfolgt. Gleichzeitig beobachteten wir eine äusserst intensive Farbänderung der Lösung. Die rötlich-gelbe schwefelsäurige Chromatlösung ändert ihre Farbe nach Einführung des Alkohols und nimmt eine intensive rotbraune Tönung an, um nach ungefähr 10–15 Minuten eine violett-grünes bzw. schmutzig-grünes Aussehen zu haben, davon abhängend wieviel Alkohol zur Reaktion kam. Die Lösung zeigt in diesem Falle die Mischfarbe des zurückgebliebenen Chromats und der sich gebildeten Chrom (III)-Verbindung.

Die Alkohol-Chromat-Reaktion in saurem Medium ist von vielen Forschern studiert und in der Literatur behandelt worden.[4–9] Sie führten ihre Untersuchungen in geringeren Schwefelsäurekonzentrationen durch, um auf diese Weise die kinetischen

* In folgenden wollen wir einfachheitshalber nur von Chromat sprechen, weil die Isopolysäurebildung mit der Erhöhung der Schwefelsäurekonzentrationen bei der Dimerisation nicht halt macht.

[1] E. SCHULEK, E. PUNGOR, und J. TROMPLER *Mikrochem. Acta* 1005 (1956).
[2] E. SCHULEK, E. PUNGOR, und J. TROMPLER *Mikrochem. Acta* 85 (1957).
[3] E. SCHULEK und P. RÓZSA *Z. anal. Chem.* **117**, 400 (1939).
[4] M. SCHWARZ *Z. Elektrochem.* **32**, 15.
[5] M. BOBTELSKY, CH. RADOVENSKY, und CHOLATNIKOV *Z. anorg. Chem.* **199**, 241 (1931).
[6] M. BOBTELSKY und RACHEL COHN *Z. anorg. Chem.* **210**, 225 (1933).
[7] W. WATENABE und F. H. WESTHEIMER *J. chem. Phys.* **17**, 61 (1949).
[8] R. SCHLACK und W. A. WATERS *J. chem. Soc.* 594, 599 (1949).
[9] M. COHN und WESTHEIMER *J. Amer. chem. Soc.* **74**, 4387 (1952).

Konstanten der Reaktion gut messen zu können. ANTONY und CHATTERJI,[10] befassten sich mit der Kinetik der Alkohol-Chromat-Reaktion und untersuchten die sich hier abspielenden Vorgänge besonders eingehend.

Sowohl ANTONY und CHATTERJI, als auch die in der älteren Literatur erschienene Arbeit von KURTENACKER[11] befasst sich mit der Abhängigkeit der Geschwindigkeitskonstante von der Säurekonzentration. Die Geschwindigkeitskonstante der Reaktion zwischen Bichromat und salpeteriger Säure enthält nach *Kurtenacker* das Quadrat der Säurekonzentration. ANTONY und CHATTERJI, stellen fest, dass sich die Geschwindigkeitskonstante der Alkohol-Chromat-Reaktion mit der Säurekonzentration linear ändert, wenn letztere klein ist, aber quadratisch, wenn sie gross ist. Nach Meinung einiger Verfasser[5–6] soll die Säure die Oxydationsreaktionen des Bichromats katalysieren. Im Falle des Jodids und des Sulfits hängt nach SCONZO[12–13] die Geschwindigkeitskonstante der Chromatreaktion mit der Hydrogenionkonzentration linear zusammen. Letzters erwähnte Verfasser führten ihre Untersuchungen bei kleinen Säurekonzentrationen durch. SNETHLAGE[14] stellte fest, dass im Falle der Oxydation von Bernsteinsäure und von Glutarsäure mittels Kaliumbichromats die Reaktionsgeschwindigkeit bei +50°C in 76,7%-iger, bei −40°C hingegen in 73,5–74,5%-iger Schwefelsäurekonzentration maximal ist. Im Intervallum von 60–100% Schwefelsäure ist die Oxydationsgeschwindigkeit in Gegenwart von Kaliumbichromat zwischen 75–78% maximal, bei 99,5% hingegen minimal.[15] SNETHLAGE[16] stellte gleichfalls fest, dass der Temperaturkoeffizient der sich zwischen Bernsteinsäure und Bichromat abspielenden Reaktion zweiter Ordnung seinen kleinsten Wert in 70%-iger Schwefelsäure hat.

Anschliessend an die kurze literarische Übersicht erwähnen wir noch folgende eigene Beobachtungen bzw. Arbeit auf dem Gebiete der Säurekonzentrationsbeeinflussung der kinetischen Reaktionen. Wir untersuchten das System Caro'sche Säure-Wasserstoffperoxyd in Gegenwart von Mangan (II)-Ionen. Es handelt sich in diesem Falle um die Oxydation des Mangan (II)-Ions mittels Caro-scher Säure.[17] Die Oxydation geht bloss dann mit grösserer Geschwindigkeit vor sich, wenn die Stabilität der Mangan (IV)-im Gegensatz zur Mangan (III)-Oxydationsstufe grösser wird. In Schwefelsäurekonzentrationen, in denen entsprechend dem SEM'schen[18] Gleichgewicht eine dominierende Mangan (III)-Bildung ermöglicht ist, sinkt die Reaktionsgeschwindigkeit zwischen Caro'scher Säure und Mangan (II). Auf Grund eingehender Untersuchungen stellten wir fest, dass die Säurekonzentration nicht direkt in den Reaktionsgang eingreift, sondern die Stabilität der einzelnen Manganoxydationsstufen in Gegenwart der anderen ändert. Es war zu erwarten, dass die Caro-sche Säure, die mit zwei Elektronen an der Reaktion teilnimmt—unter Annahme des realen Zweierzusammenstosses—nur dann das Mangan (II) oxydiert, wenn die Säurekonzentration die Bildung des Mangan (IV) in entsprechender Menge gestattet.

Diese Überlegungen, die starke Farbänderung bei der Alkohol-Chromat-Reaktion

[10] V. ANTONY und A. C. CHATTERJI *Z. anorg. Chem.* **280**, 110 (1955).
[11] A. KURTENACKER *Monatsh. Chem.* **41**, 91 (1920).
[12] A. SCONZO *Gazz. chim. ital.* **63**, 58, 70 (1933).
[13] A. SCONZO *Atti. Congr. naz. Chim. pure appl.* **5**, 1, 557.
[14] H. C. S. SNETHLAGE *Rec. Trav. chem. Pays-Bas* **56**, 605 (1957).
[15] H. C. S. SNETHLAGE *Rec. Trav. chim. Pays-Bas* **56**, 873 (1937).
[16] H. C. S. SNETHLAGE *Rec. Trav. chim. Pays-Bas* **60**, 199 (1941).
[17] E. PUNGOR und J. TROMPLER *Acta chim. Hung.* Unter druck.
[18] M. SEM *Z. Elektrochem.* **21**, 426 (1915).

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und die Angaben der Literatur liessen mit Recht darauf schliessen, dass die Säurekonzentration im Falle der Chromatoxydation die Bildung des Chrom (IV) ermöglicht.

Die aufgeworfene Frage suchten wir sowohl auf qualitativem als auch auf quantitativem experimentellem Wege zu beantworten. An Stelle des Alkohols wandten wir Ameisensäure an, um dadurch die reaktionskinetischen Stufen zu vereinfachen. Auf diese Weise erreichten wir, dass die Oxydation des organischen Stoffes in einer Stufe erfolgte. Alkohole und andere reduzierend wirkende Stoffe kamen nur bei nicht reaktionskinetischen Untersuchungen zur Anwendung.

KINETIK DER CHROMSÄUREREDUKTION

Beschreibung des Verfahrens

Im Laufe unserer kinetischen Untersuchungen wandten wir folgende Chemikalien an: umkristallisiertes Kaliumbichromat von p.a. Qualität, destillierte Schwefelsäure gleicher Qualität und Natriumformiat p.a. von E. MERCK. Die kinetischen Messungen führten wir folgendermassen durch. Nach Reaktionsbeginn massen wir die Extinktionen der einzelnen Lösungen in verschiedenen Zeitsabständen am Beckman DU Spektrophotometer bei der Wellenlänge von 440 mμ. Aus den erniedrigten Extinktionswerten konnte die Geschwindigkeitskonstante der Reaktion sowohl bei Chromat-, als auch bei Ameisensäureüberschuss bestimmt werden. Die Extinktion, des sich gebildeten Chrom (III) wurde bei den Berechnungen in Betracht gezogen. Die Reaktion zwischen Chromat und Ameisensäure konnte selbstverständlich nur bei solchen Schwefelsäurekonzentrationen kinetisch verfolgt werden, bei denen die rotbraune Farbe im Laufe der Reaktion nicht auftrat. Die diesbezüglichen Untersuchungen wurden in 40, 50, 60 und 90%-iger Schwefelsäure durchgeführt. Bei diesen Werten war die bereits erwähnte rotbraune Verfärbung in der entsprechend kleinen Reagentienkonzentration nicht feststellbar.

Die Chromatkonzentration wurde so gewählt, dass der Fehler der Extinktionsmessung möglichst klein bleibe und betrug in jedem Falle $3{,}35 \times 10^{-3}$ Mol/Lit. Die Konzentration der Ameisensäure hatte den Wert von etwa 1×10^{-2} Mol/Lit. (Einen Fall ausgenommen.) Bei Ameisensäureüberschuss nähmlich hatte die Lösung einen Gehalt von $5{,}7 \times 10^{-1}$ Mol/Lit, wie dies auch aus der Tabelle 1 ersichtlich ist.

TABELLE 1.—DIE GESCHWINDIGKEITSKONSTANTEN DER CHROMSÄUREREDUKTION MITTELS FORMIATS

Konzentration der			Geschwindigkeitskonstante k (Min^{-1} Mol^{-1} Lit.)
Schwefelsäure (g/g%)	Ameisensäure Mol/Lit.	Chromsäure* Mol/Lit.	
40	1×10^{-2}	$2{,}35 \times 10^{-3}$	$2{,}1 \pm 0{,}2$
50	1×10^{-2}	$2{,}35 \times 10^{-3}$	$9{,}3 \pm 0{,}9$
50	$5{,}7 \times 10^{-1}$	$2{,}35 \times 10^{-3}$	$8{,}7 \pm 0{,}8$†
60	1×10^{-2}	$2{,}35 \times 10^{-3}$	65 ± 5
90	1×10^{-2}	$2{,}35 \times 10^{-3}$	21 ± 4

* Die Konzentrationswerte beziehen sich auf die monomere Chromsäure.

† Nach den Angaben von Dhar, Westheimer, Antony and Chatterji hat k den Wert von 12 ± 1 bei der gleichen Ameisensäurekonzentration aber $1{,}18 \times 10^{-3}$ Mol/Lit Chromsäurekonzentration.

Ergebnisse unserer Untersuchungen

Tabelle 1 enthält die Geschwindigkeitskonstanten der zwischen Chromat und Ameisensäure sich abspielenden Reaktion in 40, 50, 60 und 90%-iger Schwefelsäure. Aus den Angaben der Tabelle ist zu ersehen, dass sich die Geschwindigkeitskonstante mit steigender Säurekonzentration rasch erhöht. Die Reaktionsgeschwindigkeit sinkt in 90%-iger Schwefelsäure, was der Beobachtung von Snethlage entspricht.

Wenn die Konzentration der einen Komponente im Gegensatz zur anderen gross genug gewählt wird und die Bestimmung der Reaktionsordnung für die jeweils in geringerer Menge vorhande erfolgt, so zeigh sich bloss dann eine Übereinstimmung der Geschwindigkeitskonstanten, falls diese nach der Gleichung einer Reaktion erster Ordnung berechnet werden. Da wir für beide Komponenten im Falle der vorher erwähnten Messmethode eine Reaktion erster Ordnung fanden, kann die Geschwindigkeit mit folgender Gleichung ausgedrückt werden:

$$v = k \cdot [\mathrm{Cr(VI)}] \cdot [\mathrm{HCOOH}]$$

Unsere Ergebnisse zeigen im Einklang zu den aus der Literatur bekannten Angaben, dass sich im Laufe der Chromatreduktion vierwertiges Chrom bilden muss, da sich die Oxydationsstufen des reduzierend wirkenden Stoffes in zwei Elektronen bzw. einem Oxygenatom unterscheiden. Wir wollten diese Feststellung nicht bloss mit reaktionskinetischen, sondern auch mit anderweitigen Messungen unterstützen. Aus Tabelle 1 ist zu ersehen, dass die Geschwindigkeitskonstante schon in 60%-iger Schwefelsäure einen hohen Wert erreicht. Mit dem weiteren Anstieg der Säurekonzentration nimmt die Geschwindigkeit der Chromatreduktion für das Auge gut bemerkbar stark zu, kann aber kinetisch nicht verfolgt werden, weil sich in etwa 70%-iger Schwefelsäure nach Zugabe des reduzierend wirkenden Stoffes das rotbraune Produkt bildet. Die Oxydation kann bei dieser Säurekonzentration als praktisch augenblicklich aufgefasst werden. Den Beweis der Bildung des vierwertigen Chroms suchten wir in 73%-iger Schwefelsäure zu bringen.

Im Laufe unserer Dampfraumanalysemessungen[1-2] stellten wir fest, dass die gasometrisch abgemessenen Methylalkoholmengen nur dann mittels Chromats reproduzierbar bestimmt werden können, wenn ein bestimmtes Chromat-Alkohol-Mengenverhältnis nicht überschritten wird. Wenn wir die dem Dampfbehälter entnommene Luft-Alkohol-Menge in schnellem Strom durch die Chromat enthaltende 73%-ige Schwefelsäure führten, so bildete sich die rotbraune Farbe augenblicklich um dann nach etwa 15 Minuten die Mischfarbe von Chrom (VI) und Chrom (III) zu geben. Diese Tatsachen, dh. die Augenblicksreaktion des Methylalkohols mit der Chromatlösung und die danach auftretende zeitlich gut verfolgbare Farbänderung sprechen dafür, dass wir es hier mit zwei Reaktionsfolgen zu tun haben. Die primäre Reaktion verläuft äusserst rasch und liefert die intermediäre Chrom (IV)-Verbindung. Da die Disproportionierung des Chrom (IV) zu Chrom (VI) und Chrom (III) eine Zeitreaktion ist, was kinetische Messungen später noch unterstrichen, so kann angenommen werden, dass der Alkohol zum grössten Teil mit dem ursprüglich anwesenden Chromat reagiert. Die Durchspülung der Chromatlösung mit Luft erniedrigt die Möglichkeit der sekundären Reaktion zwischen dem zurückgebildeten Chromat und dem nicht in Reaktion getretenen Alkohol. Abb. 1 enthält unsere diesbezüglichen Ergebnisse. An die Abszisse trugen wir die eingewogenen, an die Ordinate die titrimetrisch gemessenen Methylalkoholmengen auf. Zur Oxydation der

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einzelnen Proben wurden stets gleiche Mengen Chromat verwandt (10,00 ml 0,1 *n* $K_2Cr_2O_7$ in 73%-iger Schwefelsäure). Aus der Abbildung ist zu ersehen, dass die Alkoholmenge nur dann wiedergemessen werden kann, wenn deren Oxydation nicht mehr als 2/3 der angewandten 0,1 *n* $K_2Cr_2O_7$-Lösung in Anspruch nimmt. Wenn die Alkoholmenge mehr als 2/3 der Masslösung zur quantitativen Oxydation verbrauchen sollte, so wurden unsere Ergebnisse ungenau, dh. eszeigte sich ein Alkoholverlust. Diese Tatsachen sprechen dafür, dass sich im Laufe der Primärreaktion Chrom (IV) bilden musste, dessen Farbe wir in 73%-iger Schwefelsäure beobachten konnten.

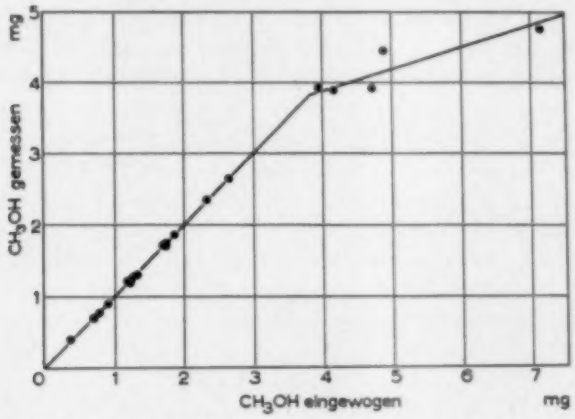

Abb. 1.—2/3 der Oxydationskraft des eingewogenen Cr(IV) entspricht 3,60 mg CH_3OH.

Aus den oben besprochenen Untersuchungsergebnissen zogen wir den Schluss, dass die Erhöhung der Schwefelsäurekonzentration in der Struktur des Chromats eine Änderung hervorruft und die Bildung des Chrom (IV) ermöglicht. Es liegt an der Hand, dass die Polymerisation der Chromsäure mit der Erhöhung der Schwefelsäurekonzentration in bestimmten Stufen fortschreitet. Um diese Tatsache zu unterstützen, wurden von uns Vorversuche betreffs der Bestimmung der Diffusionskonstante der Chromsäure in verschiedenen Schwefelsäurekonzentrationen begonnen.* Wir wollen darauf hinweisen, dass sich die Diffusionskonstante der Chromsäure in 73%-iger Schwefelsäure im Gegensatz zu niedrigeren Säurekonzentrationen stark erniedrigt.

Die Stabilität der Chrom (IV)-Verbindung sinkt in 90%-iger Schwefelsäure. Die rotbraune Farbe kann bei den in diesem Falle von uns angewandten kleinen Konzentrationen nicht beobachtet werden. Ausserdem fällt die Geschwindigkeit der Reduktion des Chromats in dieser Säurelösung (siehe die Geschwindigkeitskonstante in 90%-iger Schwefelsäure; Tabelle 1).

Aus unseren jetzigen Ergebnissen können wir den Schluss ziehen, dass die Chromsäure organische Stoffe, im allgemeinen Verbindungen die mit zwei Elektronen an der Reaktion teilnehmen, nur in solchen Schwefelsäurelösungen mit befriedigender Geschwindigkeit oxydiert, in denen die Bedingung der Chrom (IV)-Bildung gegeben ist. Die Vorversuche zur Messung der Diffusionskonstante weisen darauf hin, dass diese Bedingung in Lösungen gegeben ist, die etwa Schwefelsäuredihydrat und in

* Die diesbezüglichen Messungen führte Herr L. Hegedüs vom Elektronenmikroskopischen Institut aus, dem wir zu Dank verpflichtet sind. Mit den Ergebnissen befassen wir uns später.

diesem Medium sich gebildete Isopolychromsäure enthalten. Die Polymerisation schreitet fort und die Bedingung der Chrom (IV)-Bildung hört auf, wenn die Konzentration des Wassers weiter gesenkt wird.

UNTERSUCHUNG DER CHROM (IV)-DISPROPORTIONERUNG

Die Disproportionierung des Chrom (IV) kann mit freiem Auge beobachtet werden. Chromatlösungen in 70–85 % iger Schwefelsäure nehmen nach Zufügen des reduzierend wirkenden Stoffes sofort die charakteristische rotbraune Farbe an. Letztere ändert sich mit der Zeit und geht in die dem drei- und sechswertigen Chrom entsprechende Mischfarbe über. Es lag an der Hand diesen Farbwechsel nach der Auswahl der entsprechenden Wellenlänge am Spektrophotometer zu verfolgen. Die Messungen wurden bei der Wellenlänge von 440 mμ am Beckman DU Spektrophotometer durchgeführt.

Es musste entschieden werden, ob die gemessenen Extinktionswerte zur kinetischen Untersuchung der Chrom (IV)-Disproportionierung herangezogen werden können, da die sich gleichzeitig bildenden Chrom (III)- und Chrom (VI)-Verbindungen im selben Wellengebiet Licht absorbieren.

Seien $C_{III,t}$, $C_{III,t}$ und $C_{III,t}$ die Konzentrationen des entsprechend wertigen Chroms.

Da die Disproportionierung des Chrom (IV) mit folgender Gleichung ausgedrückt werden kann.

$$3Cr(IV) = 2Cr(III) + Cr(VI),$$

ergeben sich für die einzelnen Glieder die folgenden Differenzialgleichungen

$$-\frac{d\,C_{IV}}{dt} = k \cdot C_{IV,t} \tag{1}$$

$$\frac{d\,C_{III}}{dt} = 2/3k \cdot C_{IV,t} \tag{2}$$

$$\frac{d\,C_{VI}}{dt} = 1/3k \cdot C_{IV,t} \tag{3}$$

Wenn Gleichung (1) zwischen den Grenzen $t = 0$ und t integriert wird, so erhält man folgenden Ausdruck:

$$C_{IV,t} = C_{IV,o} \cdot e^{-kt} \tag{4}$$

und setzt diesen in Gleichung (2) und (3) ein:

$$d\,C_{III} = 2/3 \cdot k \cdot C_{IV,o} \cdot e^{-kt} \cdot dt$$

$$d\,C_{VI} = 1/3 \cdot kC_{IW;o} \cdot e^{-kt} \cdot dt$$

Wenn die Integration nun von $t = 0$ bis t durchgeführt wird, so erhält man:

$$C_{III,t} = 2/3C_{IV,o}\,(1 - e^{-kt}) \tag{5}$$

$$C_{VI,t} = 1/3C_{IV,o}\,(1 - e^{-kt}) \tag{6}$$

Die Extinktion einer Chromatlösung, die das Chrom in verschiedener Wertigkeit

enthält, kann mit folgender Gleichung ausgedrückt werden:

$$E_t = E_{IV,t} + E_{III,t} + E_{VI,t} + E^{\circ}_{IV} \tag{7}$$

wo

E_t die Extinktion der Mischung in der Zeit t,

$E_{IV,t}$ $E_{III,t}$ und $E_{VI,t}$ hingegen die Extinktion der vier-, drei- und sechswertigen Chromkomponente zur Zeit t bedeutet,

E°_{VI} aber die Extinktion des an der Primärreaktion nicht teilgenommenen sechswertigen Chroms bedeutet.

Die Konzentrationen der einzelnen Chromkomponenten können, wenn wir für sie die Gültigkeit des Lambert-Beer'schen Gesetzes annehmen, in Extinktionen umgerechnet, dh. mit diesen ausgedrückt werden. Die Gültigkeit des Lambert-Beer'schen Gesetzes kann, da wir bei etwa 10^{-3} Mol/Lit arbeiteten, angenommen werden. Die Gleichungen (4), (5) und (6) in Extinktionswerten ausgedrückt, lauten:

$$E_{IV,t} = E_{IV,t} \cdot e^{-k} \tag{8}$$

$$E_{III,t} = 2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} \cdot E_{IV,o} \cdot (1 - e^{-kt}) \tag{9}$$

$$E_{VI,t} = 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}} \cdot E_{IV,o} \cdot (1 - e^{-kt}) \tag{10}$$

Wenn man diese Ausdrücke in Gleichung (7) einsetzt und vereinfacht, so erhält man:

$$E_t - E^{\circ}_{VI} - E_{IV,o}\left(2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} + 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}}\right) = E_{IV,o}\left(1 - 2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} - 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}}\right) e^{-kt} \tag{11}$$

Wenn die Disproportionierungsreaktion theoretisch bei $t = \infty$ (praktisch in 2–3 Stunden in 73%-iger Schwefelsäure) vollständig abgelaufen ist, so erhalten wir den Extinktionswert auf Grund der Disproportionierungsgleichung mittels folgenden Ausdrucks:

$$E_{\infty} = E^{\circ}_{VI} + 2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} E_{IV,o} + 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}} E_{IV,o} \tag{12}$$

E°_{VI} kann daraus ausgedrückt und in die Gleichung (11) eingesetzt werden, die nun so das Endergebnis gibt.

$$E_t - E_{\infty} = E_{IV,o}\left(1 - 2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} - 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}}\right) e^{-kt} \tag{13}$$

Wenn wir daher zum Zeitpunkte t_1 und t_2 die Extinktion der Lösung bestimmen, können wir zur Berechnung von k folgenden Ausdruck gebrauchen

$$2{,}303 \cdot \log \frac{E_{t_1} - E_{\infty}}{E_{t_2} - E_{\infty}} = k \cdot \Delta t \tag{14}$$

Wir führten mit Hilfe dieser Formel, nach der Bestimmung der entsprechenden Extinktionswerte in 73, 75, 80 und 83%-iger Schwefelsäure und bei zwei Temperaturen, Berechnungen durch. Die Messungen bei 19,2°C konnten mit grosser Genauigkeit erfolgen, da die Zimmertemperatur etwa 20°C betrug. Bei 30°C Reaktionstemperatur war dies nicht der Fall, so dass diese Ergebnisse nur qualitativen Charakter haben.

Die Versuche wurden folgendermassen durchgeführt. Die, Schwefelsäure bestimmter Konzentration enthaltenden Chromat- und Ameisensäurelösungen wurden mit Hilfe des Ultrathermostaten auf die gewünschte Temperatur gebracht und in einem bestimmten Mengenverhältniss vermischt. Die Reaktionsdauer wurde von diesem Zeitpunkte an gerechnet. Die 1 cm Küvette des Beckman DU Spektrophotometers wurde möglichst rasch mit der Reaktionsmischung gefüllt und die Extinktion zu verschiedenen Zeitpunkten, im Vergleiche zur Schwefelsäure derselben Konzentration, gemessen. Wenn die Reaktionstemperatur von der Zimmertemperatur stark abwich, so wurde mit der jetzt beschriebenen Methode keine exakte kinetische Messung vorgenommen, weil die Temperaturbeständigkeit bei uns apparativ nicht gesichert werden konnte. (Aus diesem Grunde konnten keine energetischen Berechnungen angestellt werden. Wir wollen nach der Überbrückung der experimentellen Schwierigkeiten auf dieses Problem zurückgreifen).

TABELLE 2.—DIE GESCHWINDIGKEITSKONSTANTEN DER CHROM (IV)-DISPROPORTIONIERUNG

Schwefelsäurekonzentration (g/g%)	Temperatur (°C)	Geschwindigkeitskonstante (Min^{-1}) k
73	19,2	$0{,}12 \pm 0{,}005$
75	19,2	$0{,}11 \pm 0{,}015$
80	19,2	$0{,}064 \pm 0{,}005$
83	19,2	$0{,}048 \pm 0{,}007$
70	30	$0{,}5 \pm 0{,}1$
80	30	$0{,}2 \pm 0{,}02$

Tabelle 2 enthält die aus unseren Messergebnissen errechneten Geschwindigkeitskonstanten*. Die Angaben der Tabelle zeigen, dass die Chrom (IV)-Disproportionierung eine Reaktion erster Ordnung ist.

Der Mechanismus der Chrom (IV)-Disproportionierung kann folgendermassen erklärt werden. Das Chrom (VI) der Isopolychromsäure wird augenblicklich zu Chrom (IV) reduziert. Die Disproportionierung geht nun so vor sich, dass eine intermolekulare Umlagerung im Isopolychrom(IV) säuremolekül stattfindet (die Aktivierungsenergie dieser Reaktion beträgt etwa 15–20 Kcal). Dies hat zur Ursache, dass die Chromatome des Moleküls die Drei und Sechswertigkeit annehmen, entsprechend der schon erwähnten Reaktionsgleichung. Die Geschwindigkeit dieser Umlagerung ist unseren Messungen nach in 73%-iger Schwefelsäure maximal. Von 73% aufwärts fällt die Geschwindigkeit stätig.

BESTIMMUNG DES EXTINKTIONSKOEFFIZIENTEN DES VIERWERTIGEN CHROMS

Im Laufe dieser Untersuchungen drängte sich folgende Frage auf. Kann der dekadische molare Extinktionskoeffizient des Chrom (IV) bestimmt werden? Im folgenden wollen wir dieses Problem behandeln. Gleichung (13), die zu den oben besprochenen reaktionskinetischen Berechnungen herangezogen wurde, enthält auch den Extinktionskoeffizienten des Chrom (IV). Die Extinktion des Chrom (IV) kann in dieser Gleichung mit dem Produkt der Konzentration und des Extinktionskoeffizienten

* Bei der Berechnung der Konstanten wurde die oben abgeleitete Gleichung angewandt.

des Chrom (IV) ausgedrückt werden. (Dies kann deshalb geschehen, weil die Chrom (IV)-Konzentration etwa 10^{-3} Mol/Lit beträgt und die Gültigkeit des Lambert-Beer'schen Gesetzes in den meisten Fällen bei ähnlichen Werten zutrifft.) Wenn daher die Gleichung dementsprechend umgestaltet und in logarithmischer Form ausgedrückt wird, so erhält man:

$$\log \frac{E_t - E}{C_{IV,o}} = \log \left(\varepsilon_{IV} - 2/3\, \varepsilon_{III} - 1/3\, \varepsilon_{IV} \right) - \frac{kt}{2{,}303} \tag{15}$$

Der dekadische molare Extinktionskoeffizient des Chrom (IV) kann nur dann errechnet werden, wenn die entsprechenden Extinktionskoeffizienten des drei- und sechswertigen Chroms bekannt sind. Die Konzentration des vierwertigen Chroms zur Zeit $t = 0$ muss ebenfalls bekannt sein. Diesem Werte ($C_{IV,o}$) kann auch physikalische

Tabelle 3.—Der dekadische molare Extinktionskoeffizient des Chrom (IV) bei 440 mμ

Schwefelsäurekonzentration (g/g%)	$C_{IV,o}$ Mol/Lit	$\varepsilon_{III}^{\lambda=440}$	$\varepsilon_{VI}^{\lambda=440}$	$\varepsilon_{IV}^{\lambda=440}$
73	$2{,}11 \times 10^{-3}$	22	267	502 ± 13
75	$2{,}47 \times 10^{-3}$	22	307	502 ± 16
80	$2{,}11 \times 10^{-3}$	22	334	505 ± 15
83	$2{,}42 \times 10^{-3}$	22	344	440 ± 15

Bedeutung zugesprochen werden, weil im Gegensatz zur äusserst raschen (augenblicklichen) Reduktion des Chromats die Disproportionierung des Chrom (IV) eine langsame Reaktion ist. Die Extinktionskoeffizienten des drei- und sechswertigen Chroms können ohne jede Schwierigkeit gemessen werden. Die Bestimmung des $C_{IV,o}$-Wertes ist nach folgender Methode möglich. Gleichung (12) wird zur Bestimmung von $C_{IV,o}$ herangezogen. Wenn wir von der Extinktion des zu Reaktionsbeginn anwesenden Chromats (E^o) beide Seiten der Gleichung subtrahieren und an Stelle von $E^o - E^o_{VI}$ den Ausdruck $E_{IV,o} \frac{\varepsilon_{VI}}{\varepsilon_{IV}}$ gleichen Wertes setzen, so ergeben sich folgende Gleichungen:

$$E^o - E_\infty = E^o - E^o_{VI} - E_{IV,o}\left(2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} + 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}} \right) \tag{16}$$

$$E^o - E_\infty = E_{IV,o}\left(\frac{\varepsilon_{VI}}{\varepsilon_{IV}} - 2/3 \frac{\varepsilon_{III}}{\varepsilon_{IV}} - 1/3 \frac{\varepsilon_{VI}}{\varepsilon_{IV}} \right) \tag{17}$$

$$E^o - E_\infty = C_{IV,o}\, 2/3\, (\varepsilon_{VI} - \varepsilon_{III}) \tag{18}$$

$$\text{Daraus folgt} \quad C_{IV,o} = 3/2 \frac{E^o - E_\infty}{\varepsilon_{VI} - \varepsilon_{III}} \tag{19}$$

Wenn Gleichung (19) in (15) eingesetzt wird, erhält man den dekadischen molaren Extinktionskoeffizienten des vierwertigen Chroms bei der Wellenlänge von 440 mμ. Die diesbezüglichen Ergebnisse enthält Tabelle 3. Es ist daraus zu ersehen, dass der Extinktionskoeffizient des vierwertigen Chroms in 83%-iger Schwefelsäure sinkt, was

darauf zurückzuführen ist, dass die Geschwindigkeiten der Chrom (IV)-Disproportionierung und der Chrom (VI)-Reduktion voneinander nicht mehr in Grössenordnungen abweichen. Interessant sind die Messergebnisse an Lösungen mit 90% Schwefelsäure. Wenn hier nach der oben abgeleiteten Formel der Extinktionskoeffizient berechnet wird, so erhält man den der Chromsäure. Dieses Ergebnis steht im Einklange zu jener Beobachtung, derzufolge in den niedrigkonzentrierten Versuchslösungen bei 90%-iger Schwefelsäure die Farbe des vierwertigen Chroms nicht zu bermerken war.

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PHOSPHATES AND POLYPHOSPHATES OF THE RARE-EARTH ELEMENTS—I

THE HYDROGEN ION DISPLACEMENT METHOD FOR THE CHARACTERIZATION OF THE PHOSPHATES AND POLYPHOSPHATES OF SOME RARE EARTHS

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Abstract—Addition of sodium phosphates (and polyphosphates) to rare-earth solutions, both adjusted to a pH of 4·5, results in the precipitation of the normal phosphates (and polyphosphates) corresponding to the formulas RPO_4, $R_4(P_2O_7)_3$ and $R_5(P_3O_{10})_3$, accompanied by displacement of hydrogen ion from the respective ionic species, $H_2PO_4^-$, $H_2P_2O_7^{=}$ and $H_2P_3O_{10}^{-3}$. This displacement reaction has been evaluated for the $H_2PO_4^-$ rare-earth reaction as a method for determination of average atomic weights and has been found to give results which in general are somewhat higher than those based on the accepted oxide-oxalate ratio. Preliminary evidence is also presented to demonstrate that the trivalent rare earths form water-soluble pyrophosphato and triphosphato complexes.

EVEN though the rare earths occur most abundantly in nature in the form of the phosphate mineral monazite only a comparatively limited amount of work has been carried out to effect the preparation of the phosphates and polyphosphates of these elements by precipitation reactions from aqueous solutions. Many of the earlier investigations depended upon precipitation reactions in which a relatively basic alkali phosphate or pyrophosphate was added to the more acidic rare-earth solution. The composition of the resulting products was found to vary considerably, since competition between the hydroxide and phosphate ions for the rare-earth ions in solution invariably led to the formation of impure products.

During the course of an investigation designed to extend our knowledge of properties of the rare-earth phosphates and polyphosphates it was observed that the addition of dihydrogen phosphate to the rare-earth salt at the same pH resulted in the precipitation of the phosphate accompanied by a marked increase in the acidity of the solution. Back titration of the liberated hydrogen ion indicated that this reaction could be represented by the following equation:

$$R^{+3} + H_2PO_4^- \rightarrow RPO_4 \downarrow + 2H^+ \qquad (1)$$

This finding suggested that it might be possible to determine the average atomic weight of a rare-earth mixture by an evaluation of the oxide-hydrogen ion ratio.

$$R_2O_3/4H^+ = \text{wt. of rare-earth oxide/(normality of NaOH) (vol.) (0·001008)}$$

Such a procedure would possess distinct advantages with respect to simplicity over the widely used method based upon the oxide-oxalate ratio[1] and would constitute a useful supplementary method to spectrophotometric and radioactive tracer techniques now employed to follow the separation of the rare earths by ion exchange.

The hydrogen ion displacement method has been used by various investigators

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[1] D. W. PEARCE, G. L. BARTHAUER, and R. G. RUSSELL *Inorg. Synth.* II, 58 (1946).

for the determination of the constitution of metallic phosphates.[2,3] This method has also been used for the alkalimetric determination of phosphoric acid and phosphates[4,5,6] and constitutes in principle the basis of a procedure for the analysis of mixtures of pyro- and tri-phosphate.[7]

It is well known that phosphoric and polyphosphoric acids contain only one strongly acidic hydrogen atom per phosphorus atom in the acid molecule. Acid-base titration curves have demonstrated that the respective phosphate and polyphosphate ions, $H_2PO_4^-$, $H_2P_2O_7^{=}$ and $H_2P_3O_{10}^{=}$ are best defined at a pH of approximately 4·5. Precipitates consisting essentially of the normal phosphates and polyphosphates, RPO_4, $R_4(P_2O_7)_3$ and $R_5(P_3O_{10})_3$ were obtained when phosphate (and polyphosphate) solutions were added to rare-earth solutions, both adjusted to a pH of 4·5. The liberated hydrogen ion was determined by back-titration with standard base. The compositions of the precipitates were verified in some cases by analysis and indirectly by appropriate conductimetric titrations. Conductimetric titrations also revealed the formation of pyrophosphate and triphosphate complexes of the trivalent rare earths at higher pH values and in the presence of excess polyphosphate ion. These polyphosphate complexes of the rare-earth elements will be the subject of a later communication.

Results of titrations employing various rare earths and the dihydrogen phosphate ion indicate that values for atomic weights are somewhat higher than those obtained using the more widely accepted oxide-oxalate procedure. However, the simplicity of the method does give it utility and suggests its employment for control analyses in following separation procedures. Like all other methods for the determination of average atomic weights the new procedure is subject to the errors occasioned by formation of tetravalent rare-earth oxides upon ignition.

EXPERIMENTAL

The same experimental approach was used for the determination of displaced hydrogen ion resulting from the addition of excess phosphate, pyrophosphate or triphosphate to solutions of various rare-earth salts. Known weights of rare-earth oxides were dissolved in dilute hydrochloric acid. The hydrogen ion concentrations of the resulting solutions were adjusted to a pH of 4·5 with sodium hydroxide, using a Beckman Model G pH meter. Standard solutions of the sodium phosphate (or polyphosphate) were also adjusted to a pH of 4·5. An excess of the phosphate (or polyphosphate) solution, varying from 10 to 100 per cent, was added dropwise with constant stirring to the rare-earth solution. The displaced hydrogen ion was then determined, usually within one half-hour after the addition of the phosphate solution, by back-titration to pH 4·5 with standard base.

All rare-earth samples used in this investigation were checked for average atomic weights by the well-known oxide-oxalate procedure, using permanganate or cerate solutions* for determination of

* Use of cerate in place of permanganate does not appear to have been evaluated previously. A possible objection to the employment of cerate for this purpose lies in the contamination of purified rare-earth samples by cerium, if recovery of materials used for analysis is essential. Statistical studies (see thesis by A. G. BUYERS[8]) demonstrated that use of either permanganate or cerate leads to completely reproducible results for average atomic weight values. Cerate solutions were prepared by dissolving an amount of hexanitratocerate to give an approximately 0·1 normal solution of Ce(IV) in 2N $HClO_4$. Sodium oxalate was used for subsequent standardization of the cerate solutions, using nitro-ferroin as indicator. The rare-earth oxalates were dissolved in 2N $HClO_4$ and the resulting solutions titrated with standard cerate, again using nitro-ferroin as indicator.

[2] J. FISCHER and G. KRAFT *Z. anal. Chem.* **149**, 34 (1956).
[3] W. RATHJE *Ber. dtsch. chem. Ges.* **74B**, 357 (1941).
[4] G. BRUNISHOLZ *Helv. chim. acta* **30**, 2028 (1947).
[5] A. SAUFOURCHE and B. FOCET *Bull. Soc. chim. Fr.* (4) **53**, 963 (1933).
[6] E. RANKE-MADSEN and T. KJAEGARD *Acta chem. Scand.* **1**, 735 (1953).
[7] R. N. BELL *Analyt. Chem.* **19**, 97 (1947); See also *Inorg. Synth.* **III**, 85 (1950).
[8] A. G. BUYERS Thesis, University of Illinois, Urbana, Illinois (1950).

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oxalate. These values were used to calculate molarities of rare-earth solutions for all studies entailing reactions with phosphates and polyphosphates. The present investigation was limited to a study of the more common rare-earth elements.

For further characterization of the identities of the rare-earth phosphates and polyphosphates prepared by these precipitation reactions, recourse was had both to gravimetric procedures and to conductimetric titrations. Elemental analysis of a number of the precipitates was undertaken to verify their compositions. Product weights obtained under varying conditions of precipitation, ignition and hydrolysis were determined where appropriate.

For conductimetric titrations, standard sodium phosphate or polyphosphate solutions were prepared by dissolving reagent grade or specially prepared salts in water and analysing for the particular phosphate by applicable analytical methods.[7] Conductimetric titrations were carried out using a 250 ml cell immersed in a thermostatic bath maintained at 25°C. The cell constant was not determined since conductance values were relative throughout a given titration. Smooth platinum electrodes in conjunction with a Leeds-Northrup conductivity bridge assembly (No. 4866) were used for measuring conductance.

Rare-earth orthophosphate conductimetric titration studies were carried out by introducing increasing amounts of the phosphate solution into the rare-earth chloride solution, diluted to be approximately 20 times less concentrated than the titrant in order to reduce dilution effects during titration. Pyro- and tri-phosphate titrations were performed in a similar fashion. To establish formation of soluble complexes in these latter cases the titration order was reversed and the phosphate solution titrated with standardized rare-earth solutions.

DISCUSSION AND RESULTS

Orthophosphates of the rare earths

Representative data obtained by the application of the technique of measuring the acidity released when solutions of various rare earths were allowed to react with excess sodium dihydrogen phosphate solutions, both adjusted to a pH of 4·5, are summarized in Table 1.

TABLE 1.—RARE-EARTH ORTHOPHOSPHATES

Element	Weight oxide (g)	Moles $R^{+3} \times 10^{-3}$	Standard base 0·1 N (ml)	Moles $H^{+} \times 10^{-3}$	Ratio H^{+}/R^{3+}	Average atomic weight	
						H^{+} displacement method	Oxalate-permanganate method
La	0·1215	0·747	14·71	1·471	1·97	141·2	138·4
	0·1416	0·869	17·13	1·712	1·97	141·3	139·0
Nd	0·1591	0·945	18·63	1·863	1·97	146·8	144·4
	0·1591	0·945	18·65	1·865	1·97	146·6	144·5
Sm	0·1395	0·797	16·07	1·607	2·02	149·6	150·6
	0·0965	0·552	10·99	1·099	1·99	151·6	150·3
Gd	0·1149	0·638	12·72	1·272	1·99	156·6	156·1
	0·1097	0·608	12·14	1·214	1·99	156·7	156·1
Y	0·1250	1·101	21·57	2·157	1·96	91·9	86·9
	0·1264	1·112	21·91	2·191	1·97	91·4	87·4

The data disclose that the predominant reaction can be represented by equation (1). Values for displaced acidity were found in general to be slightly less than demanded by theory. The corresponding average atomic weights are therefore somewhat higher than values obtained by the accepted oxide-oxalate procedure.

In order to resolve this discrepancy, the precipitated phosphates were removed by

TABLE 2.—PRECIPITATION OF NEODYMIUM PHOSPHATE

Moles $Nb^{3+} \times 10^{-3}$	Weight of precipitate ignited at 900°C (g)	Theoretical weight $NdPO_4$ (g)
0·751	0·1821	0·1797[a]
0·751	0·1829	0·1797[a]
0·751	0·1826	0·1797[b]
0·751	0·1822	0·1797[b]
0·751	0·1854	0·1797[b]
0·751	0·1853	0·1797[b]

[a] Precipitates removed immediately after back-titration; washed with dilute ammonium chloride solution.

[b] Rare-earth and phosphate solutions mixed in strongly acid solution. pH raised to a point just below incidence of precipitation. Urea and bromphenol added. Heated until indicator changed colour in pH range 3·0–4·6.

filtration and ignited at 900° and weighed. Neodymium phosphate was also prepared by slow precipitation from a strongly acid solution, containing both Nd^{+3} and PO_4^{-3} ions, by adding urea, the latter serving by hydrolysis to raise the pH slowly. It was hoped that the precipitates obtained under these conditions might be more definitely crystalline than those obtained by direct addition of phosphate to neodymium solutions at a pH of 4·5. Typical data are given in Table 2.

It is interesting to note that the weights of the ignited precipitates are in all instances slightly higher than demanded by theory. Powder patterns of ignited precipitates were found to be identical with those obtained from finely ground monazite sand in which the rare earths exist as orthophosphate. The gravimetric data suggest limited formation of rare-earth dihydrogen phosphate or rare-earth monohydrogen phosphate, $R(H_2PO_4)_3$ or $R_2(HPO_4)_3$. On ignition, these would be expected to give rare-earth metaphosphate or pyrophosphate, respectively. The formation of such compounds would account for the low values observed for displaced hydrogen ion and also the high values for weights of ignited products.

However, the results of average atomic weight determinations by the hydrogen ion displacement procedure indicate that the experimental hydrogen ion–rare-earth ratio is nearly that demanded by equation (1). It was considered entirely possible that experimental ratios lower than theoretical could be accounted for by the gelatinous nature of the precipitates. A precipitate of this type might be expected to adsorb foreign ions. Addition of competitive adsorption agents and digestion of the precipitates prior to filtration did not give better results. Additional experimental work was also undertaken to overcome this slight discrepancy by various modifications in the procedure. These changes entailed (1) maintenance of constant

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pH conditions during precipitation with phosphate reagent by concurrent addition of standard base; (2) precipitation in hot solution by simultaneous addition of rare-earth solution, phosphate reagent and standard base;* (3) reversal of order of addition. Since none of these modifications of the procedure appeared to make any difference in the results obtained, it seems plausible that formation of a small amount of rare-earth hydrogen phosphate must be considered as a reasonable explanation of the observed results.

Conductimetric titrations were also undertaken to further verify the nature of the precipitates obtained under varying conditions, especially since such a procedure had already been found applicable in a number of other instances, such as (1) the mechanism of silver phosphate precipitation;[9] (2) formation of basic phosphates in the precipitation of lanthanum phosphate with various orthophosphate reagents[10] and in the determination of the nature of precipitates formed when solutions of ferric and orthophosphate ions are allowed to react.[11] For the rare-earth phosphates proof of formation of normal rare-earth phosphates as precipitation products in aqueous solution was obtained by the conductimetric titration of rare-earth ion with di- and tri-sodium phosphates. For titration of rare earth with disodium monohydrogen phosphate, a rise in conductance was observed with a peak corresponding to the precipitation of the normal phosphate and the liberation of one hydrogen ion in accordance with the equation:

$$R^{+3} + HPO_4^{=} \rightarrow RPO_4 \downarrow + H^+ \qquad (2)$$

The conductance was then found to drop as more hydrogen phosphate was added to correspond to the reaction:

$$HPO_4^{=} + H^+ \rightarrow H_2PO_4^- \qquad (3)$$

The essential completion of this second reaction was indicated by a second inflection point, after which the conductance again rose as a still greater excess of hydrogen phosphate was added to the solution. Titration of neodymium chloride solution with trisodium phosphate was shown to produce only one inflection point corresponding to the completion of the precipitation of an essentially normal phosphate of the rare earth. None of the conductance data, however, was of sufficient accuracy to determine if the resulting phosphates were contaminated with other species. It is obvious, however, that titration of a rare-earth solution with trisodium phosphate would lead to a product which could be considered a basic phosphate due to competition of the rare-earth ion both for phosphate and hydroxide ions formed by hydrolysis of the trisodium phosphate in aqueous solution.

Pyrophosphates of the rare earths

The hydrogen ion displacement procedure employed successfully for the characterization of orthophosphates was next applied to a study of the pyrophosphates

* This latter procedure had been used by RATHJE[3] as an analytical method for the quantitative determination of other metals. RATHJE had observed that more crystalline and readily filterable phosphate precipitates could be obtained under such circumstances. However, it might be pointed out that the data presented by RATHJE do not indicate that this method is adaptable as an exact quantitative procedure.

[9] W. HUBICKI *Ann. Univ. M. Curie-Sklodowska*, Sec. AA, **2**, No. 9, 153 (1947); cf. *Chem. Abstr.* **43**, 6931 (1949).

[10] W. HUBICKI *Ibid.* Sec. AA, **2**, No. 11, 186 (1947); cf. *Chem. Abstr.* **43**, 6535 (1949).

[11] W. HUBICKI *Ibid.* Sec. AA, **2**, No. 10, 167 (1947); cf. *Chem. Abstr.* **43**, 6931 (1949).

of the rare earths. Again, the rare earth solution adjusted to pH 4·5 was treated with a pyrophosphate solution adjusted to the same pH. Under these circumstances, the reaction represented by equation (4) might be expected to take place.

$$4R^{+3} + 3H_2P_2O_7^{=} \rightarrow R_4(P_2O_7)_3 + 6H^+ \qquad (4)$$

Representative experimental data are given in Table 3. The procedure was modified for the last four experiments in order to determine the effect of room temperature digestion upon the nature of the precipitates and upon the accuracy of the results for

TABLE 3.—PRECIPITATION OF NEODYMIUM PYROPHOSPHATE

pH	Moles Nd^{3+} $\times 10^{-3}$	Standard base 0·1N (ml)	Moles H^+ $\times 10^{-3}$	Ratio H^+/Nd^{3+}
3·8	2·040	28·24	2·824	1·38[a]
4·5	0·751	10·96	1·096	1·46[a]
4·5	0·951	13·40	1·340	1·41[a]
5·9	2·040	24·40	2·440	1·20[a]
4·5	0·815	11·82	1·182	1·45[b]
4·5	0·751	11·19	1·119	1·49[c]
4·5	0·951	13·81	1·381	1·45[d]
4·5	0·951	13·92	1·392	1·46[e]
4·5	0·951	14·26	1·426	1·50[f]

[a] Immediate titration after precipitation.
[b] Titrated after standing overnight.
[c] Titrated after standing 1 hr.
[d], [e], [f] Molar ratio of $Nd^{+++}/H_2P_2O_7$ = varied from 4/4, 4/5, to 4/6, respectively.

displacement of acidity. Here again, the precipitates were highly gelatinous in nature, and hydrogen ion–rare-earth ratios were found to be slightly less than demanded by equation (4).

It was found, however, that if the excess pyrophosphate used to bring about precipitation of neodymium pyrophosphate is increased markedly, H^+/Nd^{+3} ratios approaching theoretical can be achieved (Table 3). This suggested incomplete precipitation of the rare earth, which was verified by adding just slightly more than the theoretical quantity of pyrophosphate to the neodymium solution. The precipitate was then removed and oxalate added to the filtrate. A significant quantity of neodymium oxalate was precipitated, corresponding to approximately 3 per cent of the amount of neodymium used initially.

The neodymium pyrophosphate precipitate obtained by this reaction was filtered, washed with water and alcohol and dried at 110° to constant weight. The product was a light pink powder and was found upon analysis to correspond to the formula: $Nd_4(P_2O_7)_3.6H_2O$ (Found: Nd, 47·8; P, 15·38. Calc. Nd, 47·81; P, 15·40).

It was also noted that digestion of the precipitated rare-earth pyrophosphates suspended in their own mother liquor at higher temperatures prior to back-titration to a pH of 4·5 yielded hydrogen ion–rare-earth ratios consistently higher than demanded by theory. This suggested that hydrolysis of the pyrophosphate would

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occur quite readily in the acid solutions with formation of the orthophosphate. This supposition was verified by a gravimetric study of products precipitated at ordinary temperatures and those obtained after digestion at higher temperatures. In a typical experiment four aliquots containing $7{\cdot}51 \times 10^{-4}$ mole Nd^{+3} were treated with excess dihydrogen pyrophosphate. The precipitates were filtered and then ignited for at least 4 hr.

Actual weights in grammes of 0·2109, 0·2153, 0·2120, and 0·2104 are to be compared with the theoretical weight for $Nd_4(P_2O_7)_3$ of 0·2065. In these instances, continued ignition gave evidence of slight but definite losses in weight up to periods of 24 hr, but even after this time weights of products were still slightly higher than demanded by theory.

Four aliquots each containing $7{\cdot}51 \times 10^{-4}$ moles, Nd^{+3} and an excess of dihydrogen pyrophosphate, then digested at the boiling point, gave products weighing 0·1835, 0·1838, 0·1875, and 0·1827 g, compared with a theoretical weight of $NdPO_4$, 0·1799 g. This finding demonstrates that digestion of pyrophosphate precipitates at higher temperatures in the presence or even in the absence of excess of the precipitating agent but at the indicated pH causes significant hydrolysis of the pyrophosphate to the orthophosphate.

Conductimetric titrations demonstrated that normal rare-earth pyrophosphates as well as soluble rare-earth pyrophosphato complexes are formed. Addition of a standard solution of tetrasodium pyrophosphate to a solution of neodymium chloride is accompanied by precipitation of the rare-earth pyrophosphate. An inflection point is observable at a $P_2O_7^{-4}$:Nd^{+3} ratio between 0·7–0·8 corresponding to the formation of the normal pyrophosphate. A reverse titration entailing addition of neodymium salt solution to excess of pyrophosphate ($Na_4P_2O_7$) gave no initial precipitate until the pH had dropped to about 7·5, thus suggesting the formation of a pyrophosphato complex under these circumstances. Qualitatively, it was also observed that a pyrophosphate precipitate removed from the solution and then treated with an excess of pyrophosphate would go into solution in the pH range 8 to 9.

Triphosphates of the rare earths

The path of the reaction between solutions of triphosphate and those of rare-earth chlorides was also investigated with both solutions adjusted to a pH of 4·5. These data (Table 4) disclose that the primary reaction can be represented by the following equation:

$$5R^{+3} + 3H_2P_3O_{10}^{-3} \rightarrow R_5(P_3O_{10})_3 + 6H^+ \qquad (5)$$

The very gelatinous precipitates of neodymium triphosphate were also digested (a) in their mother liquors at steam bath temperatures for 12 hr, and (b) suspended in distilled water adjusted to pH 4·5. Representative data are included in Table 4 and disclose that considerable hydrolysis had occurred in both instances, again making it impossible to attempt formation of more readily filterable precipitates by digestion either at room temperatures or at higher temperatures.

The known instability of the triphosphate ion in the acid range made it necessary to use such solutions immediately after adjustment to a pH of 4·5, but even in these instances values somewhat higher than the theoretical ratio of 1·2 were obtained,

suggesting that triphosphate would not be suitable for use in determining the average atomic weights of rare-earth mixtures. It should be pointed out, however, that the precipitates obtained under these circumstances consist essentially of the normal rare-earth triphosphates.

The formation of the normal rare-earth triphosphate was also demonstrated conductimetrically. The inflection point was found to correspond essentially to an $Nd:P_3O_{10}$ molar ratio of 5:3. It was now noted, however, that the addition of excess

TABLE 4.—PRECIPITATION OF NEODYMIUM TRIPHOSPHATE

Moles Nd^{3+} $\times 10^{-3}$	Standard base 0·1N, ml	Moles H^+ $\times 10^{-3}$	Ratio H^+/Nd^{3+}
1·364	16·45	1·645	1·21
0·951	11·42	1·142	1·20
0·951	11·44	1·144	1·20
0·815	15·50	1·550	1·90[a]
0·751	14·40	1·440	1·92[b]
0·751	14·40	1·440	1·92[c]
0·751	14·30	1·430	1·90[d]

[a] Digested 16 hr on steam bath prior to titration.
[b] Digested 48 hr on steam bath prior to titration.
[c] Digested 92 hr on steam bath prior to titration.
[d] Refluxed 19·5 hr prior to titration.

pentasodium triphosphate, thus causing the pH to rise above 7·5, caused the precipitates to go into solution. That a rare-earth triphosphato complex is formed was indicated, furthermore, by a reverse titration in which a considerable quantity of neodymium chloride could be added before any evidence of formation of precipitate was observable. Such conductimetric titration curves gave no evidence of any particular inflection point which might give a clue as to the nature of the triphosphato complex in the solution. The stability of such a complex is apparently a function of pH rather than of the triphosphate-neodymium ratio.

A more thorough study of the rare-earth pyrophosphate and triphosphate complexes will be the subject of a forthcoming publication.

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More detailed data concerning the statistical evaluation of the hydrogen ion displacement procedure as a method for the determination of the average atomic weights of rare earths is to be found in the thesis by A. G. BUYERS, University of Illinois, June, 1950.

It is a pleasure for one of us (E. G.) to acknowledge his indebtedness to the Rockefeller Foundation for a fellowship which made it possible for him to participate in the above investigation and to spend the 1956–57 academic year at the University of Illinois.

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THE USE OF DIOCTYL PHOSPHORIC ACID EXTRACTION IN THE ISOLATION OF CARRIER-FREE ^{90}Y, ^{140}La, ^{144}Ce, ^{143}Pr, AND ^{144}Pr*

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Abstract—Tracer-level cerium has been oxidized to the tetravalent state and shown to be preferentially extracted from a 10 M HNO_3 aqueous phase into a 0·75 M, or 0·30 M, solution of di(2-ethyl hexyl) orthophosphoric acid in *n*-heptane. In this system the ratio of the K for Ce(IV) to that for Ce(III) is greater than 10^6, and the K for Ce(IV) is much greater than that for any trivalent lanthanide.

This system has been utilized to purify ^{144}Ce with respect to lanthanide contaminants, including its ^{144}Pr daughter, and to prepare a highly-purified gross sample of natural cerium for neutron bombardment in the preparation of ^{143}Pr. It has been used also in the isolation of ^{143}Pr and ^{144}Pr products for tracer studies and for half-life determinations. A decontamination factor, with respect to the parent ^{144}Ce, greater than 10^7 was obtained for a ^{144}Pr sample isolated and prepared for counting in a period of less than 10 min.

Other di(2-ethyl hexyl) orthophosphoric acid systems employing dilute HCl or HNO_3 as the opposing phase have been used for separating ^{90}Y from its ^{90}Sr parent and for separating ^{140}La from its ^{140}Ba parent and from contaminant ^{90}Sr–^{90}Y. Decontamination factors greater than 10^7 have been obtained in both separations, the total processing times being less than 15 min.

The following new half-life values have been obtained: ^{90}Y, 63·97 ± 0·1 hr; ^{140}La, 40·27 ± 0·05 hr; ^{143}Pr, 13·59 ± 0·04 day; and ^{144}Pr, 17·27 ± 0·04 min.

IN AN extension[1] of the initial study[2] of the partition behaviour of the lanthanides and yttrium in the system tri-*n*-butyl orthophosphate–nitric acid, it became necessary to isolate ^{90}Y, ^{140}La, ^{144}Ce, and ^{143}Pr carrier-free and in extremely high purity with respect to extraneous radioactivity. The present study reports a solution to this problem. In order to establish, rapidly, the degree of purification of tracer-level Pr separated from gross Ce, ^{144}Pr was included in the investigation.

In establishing the purity of the separated nuclides, new data for the half-lives of ^{90}Y, ^{140}La, ^{143}Pr, and ^{144}Pr were obtained. A procedure for the separation of tracer-level Ce from all other lanthanides was also devised.

The separations procedures are based upon the facts that in properly chosen di(2-ethyl hexyl) orthophosphoric acid–mineral acid systems, the relative partitions are such that the organic phase preferentially extracts: (A) Any tetravalent lanthanide, or actinide, as opposed to any trivalent lanthanide or actinide,[3] (B) both Y(III) and La(III) as opposed to both Sr(II) and Ba(II), and (C) Y(III) as opposed to La(III).[4]

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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EXPERIMENTAL

General. The beta-active nuclides 28 yr ^{90}Sr + 64·0 hr ^{90}Y, 12·8 day ^{140}Ba + 40·2 hr ^{140}La, 285 day ^{144}Ce + 17 min ^{144}Pr, 2·6 yr ^{147}Pm, and (13,16) yr ^{152,154}Eu were obtained from the Isotopes Division of the Oak Ridge National Laboratory. Beta-active 129 day ^{170}Tm was obtained from D. C. STEWART of A.N.L. (All half-life values given above are taken from *General Electric Chart of the Nuclides.*[9])

A mixture of the mono- and di-octyl orthophosphoric acids (2-ethyl hexyl isomers) was obtained from Victor Chemical Works. Di(2-ethyl hexyl) orthophosphoric acid, symbolized as HDEHP, was isolated from this mixture by a modification, reported by PEPPARD, MASON, MAIER, and DRISCOLL,[4] of the method of STEWART and CRANDALL.[5] A total of three purification cycles were used. This purified HDEHP was used in toluene diluent, except in the cerium studies in which *n*-heptane was used as diluent.

The distribution ratio, K, of a specific nuclide, defined as the concentration of nuclide in the upper divided by the concentration of nuclide in the lower of two equilibrated sensibly-immiscible liquid phases, was determined in the manner previously reported.[1,4] All data were obtained at 22 ± 2°C. The data are sufficiently precise to establish approximate concentration dependencies with respect to acid and solvent.

In the separations experiments, the organic and aqueous phases were agitated, in a small glass-stoppered cylinder, and the separated phases moved from cylinder to cylinder by means of a small transfer pipette made by drawing out a portion of 12 mm diameter glass tubing to a long, narrow, thin-walled neck, leaving a bulb of 1–5 ml capacity. These pipettes were filled and emptied by means of a hypodermic syringe attached to the pipette by a short rubber coupling. A new pipette was used for each transfer.

Half-life determinations. An aliquot of the purified product phase was evaporated on a small platinum disc to be counted in an end-window proportional counter. At the same time a much larger aliquot of the same solution was evaporated on a second platinum disc. This second disc was set aside for later counting in determining the purity of the sample.

In the beta counting involved in the determination of all half-lives other than that of ^{144}Pr, the "sample count" was followed immediately by a "standard count" in the same counter, the standard being a ^{90}Sr–^{90}Y sample which had been evaporated on a platinum disc 17 months previously. Each of the discs was fastened securely to a close-tolerance aluminium shelf sliding horizontally so that positioning of the sample and standard was highly reproducible.

Following corrections for the decay of the standard, assuming a ^{90}Sr half-life of 28 years, the data were normalized, then corrected for coincidence losses which, for the particular counter employed, was done by use of the expression:

$$T = C + 8{\cdot}5 \times 10^{-6}C^2, \tag{1}$$

where C is the normalized registered counting rate, and T is the counting rate as used in the half-life calculations. The data were treated by least-squares analysis.

Owing to the short half-life of ^{144}Pr, the above procedure was not applicable. Consequently, the accumulated-count procedure was used, without removal of sample from the chamber. A standard ^{90}Sr–^{90}Y plate, counted immediately before and after the determination, showed only a statistical variation. An electronic registering device which automatically printed, on a continuous paper roll, the total elapsed time coincident with the addition of a pre-determined increment of counts to the register was used.

In the absence of coincidence losses, the data would be treated by use of the following expression:

$$\log (A_\infty - A_t) = \log A_\infty - (0{\cdot}30103/t_{1/2})t, \tag{2}$$

where A_t is the accumulated count at time t and A_∞ at infinite time. Introducing equation (1), the following expression may be derived:

$$A_t = R_t + (2{\cdot}95 \times 10^{-6}A_\infty^2/t_{1/2})[1 - e^{-(1{\cdot}3863/t_{1/2})t}], \tag{3}$$

where R_t is the accumulated count, at time t, as registered.

From equation (3), both A_∞ and A_t may be calculated for use in equation (2). Using $\log (A_\infty - A_t)$ and t as variables, a least-squares analysis was used to calculate the half-life.

[5] D. C. STEWART and H. W. CRANDALL, *J. Amer. chem. Soc.* **73**, 1377 (1951).

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Isolation of ^{90}Y. A ^{90}Sr–^{90}Y source material, greater than 14 months old, dating from the time of isolation from mixed fission products, as chloride is converted by evaporation followed by dissolution to an aqueous 0·1 M HCl feed of 2 ml volume. This feed is contacted successively with three 2 ml portions of 1·5 M HDEHP and one 2 ml portion of toluene to rid the source of traces of ^{91}Y, ^{147}Pm, etc. Following a suitable period for growth of ^{90}Y, the purified feed is contacted successively with a 2 ml portion of 1·5 M HDEHP and a 2 ml portion of toluene, then set aside for lateruse. The resultant pregnant HDEHP phase is scrubbed with four 2 ml portions of 0·1 M HCl to remove traces of ^{90}Sr, The scrubbed HDEHP phase is diluted with a 2 ml portion of toluene and the ^{90}Y removed by re-extraction into a 2 ml portion of 5 M HCl. This aqueous product is contacted with a 2 ml portion of toluene to remove traces of HDEHP. The yield of ^{90}Y is greater than 95 per cent, and the decontamination factor with respect to ^{90}Sr is greater than 10^7. The total processing time, beginning with the contacting of the purified feed with HDEHP, is less than 15 min.

Isolation of ^{140}La. A ^{140}Ba–^{140}La source is converted to an aqueous 0·05 M HCl feed material. A 2 ml portion of this feed is contacted successively with three 2 ml portions of 1·5 M HDEHP and one 2 ml portion of toluene to rid the feed of traces of ^{91}Y, ^{144}Ce, ^{147}Pm, etc. Following a suitable period for growth of ^{140}La the purified feed is contacted successively with a 2 ml portion of 1·5 M HDEHP and a 2 ml portion of toluene, then set aside for further use. The pregnant HDEHP phase is scrubbed with four 2 ml portions of 0·05 M HCl to remove traces of ^{140}Ba (and ^{90}Sr). The ^{140}La is removed from the HDEHP phase by contacting with a 2 ml portion of 0·5 M HCl. This aqueous re-extract is then contacted successively with two 2 ml portions of 1·5 M HDEHP (to remove ^{90}Y) and one 2 ml portion of toluene. The yield of ^{140}La is greater than 80 per cent, and the decontamination factor with respect to ^{140}Ba is greater than 10^7. The total processing time, beginning with the contacting of the purified feed with HDEHP is less than 15 min.

Preparation of cerium for neutron bombardment. A 100 ml portion of feed, 10 M in HNO_3 and containing 10 g of ceric ammonium nitrate (G. Frederick Smith Chemical Co.) is contacted with 100 ml of 0·75 M HDEHP (*n*-heptane diluent). The pregnant HDEHP phase is contacted successively with ten 100 ml portions of 10 M HNO_3. All of the foregoing contact times are approximately one minute. The scrubbed HDEHP phase is contacted with a mixture of 100 ml of 10 M HNO_3 and 10 ml of 30 per cent H_2O_2 for a 10 min period. The pregnant aqueous phase is contacted with a 100 ml portion of *n*-heptane to remove traces of HDEHP and heated to destroy H_2O_2. After evaporation to dryness, a weighed quantity of the powder is transferred to a quartz tube and the tube and contents baked to remove traces of moisture.

Isolation of ^{143}Pr *from a neutron-bombarded cerium sample.* An oxidizing solvent is prepared as follows. A portion of 0·75 M HDEHP (*n*-heptane diluent) is contacted with three equal-volume portions of a freshly-prepared aqueous phase 10 M in HNO_3 and 1 M in $KBrO_3$. The bombarded sample, dissolved in 5 ml of 10 M HNO_3, is contacted successively with five 5 ml portions of freshly-prepared oxidizing solvent and one 5 ml portion of *n*-heptane. All of the foregoing contact times are 30 sec. The resulting aqueous phase contains product ^{143}Pr with less than one part in 10^7 of long-lived beta activity.

The cerium is returned to an aqueous phase to be stored until the ^{144}Ce has decayed to a suitably low level at which time the cerium is again extracted as Ce(IV), the extract scrubbed to remove traces of ^{143}Pr, and the cerium returned to an aqueous phase to be used in tracer studies.

Isolation of ^{144}Pr *from a* ^{144}Ce–^{144}Pr *source.* The ^{144}Ce–^{144}Pr sample, in 5 ml of freshly-prepared Feed-1, 10 M in HNO_3 and 1 M in $KBrO_3$, is contacted with a 5 ml portion of 0·75 M HDEHP (*n*-heptane diluent). The pregnant HDEHP phase is contacted successively with three 5 ml portions of an aqueous scrub 10 M in HNO_3 and 1 M in $KBrO_3$ and one 5 ml portion of aqueous re-extractant 10 M in HNO_3 and 1 M in H_2O_2. This aqueous product is contacted with 5 ml of *n*-heptane to remove traces of HDEHP. The foregoing procedure serves to separate Ce from ^{147}Pm, ^{91}Y, etc.

Following a suitable period for regrowth of ^{144}Pr, the product is converted to 2 ml of Feed-2 which is 10 M in HNO_3 but does not contain $KBrO_3$. This Feed-2 is contacted successively with five 2 ml portions of freshly-prepared oxidizing solvent, prepared as described in the *isolation of* ^{143}Pr section, and one 2 ml portion of *n*-heptane. In the separation made for the ^{144}Pr half-life determination, an aliquot of the product was evaporated on a platinum disc and beta counting begun within 10 min of the initial contacting of Feed-2. The decontamination factor with respect to ^{144}Ce was shown to be greater than 10^7.

Determination of ^{90}Sr *and* ^{140}Ba *K values.* By obvious modifications of the procedures described

for the isolation of ^{90}Y and ^{140}La, their respective parent activities were purified with respect to daughter activities and radioactive ^{147}Pm, ^{91}Y, etc. Immediately following the final phase separation, the product ^{90}Sr (or ^{140}Ba) was used in a K determination. In general, these determinations could be carried to the point of phase separation within a 5 min period beginning with isolation of product. The data obtained were confirmed by a second beta-counting of the samples, following the proper period of growth of daughters.

Determination of ^{144}Ce *K value*. The purified ^{144}Ce–^{144}Pr mixture was used in the determination. Aliquots of the equilibrated phases were evaporated on platinum discs to be assayed for beta activity following re-establishment of equilibrium with the ^{144}Pr daughter.

RESULTS AND DISCUSSION

The distribution ratios for Y(III) and trivalent lanthanides from dilute aqueous mineral acid into dilute HDEHP in a carrier solvent have been shown, by PEPPARD, MASON, MAIER, and DRISCOLL,[4] to be inversely third-power dependent upon the aqueous acid concentration and directly third-power dependent upon the HDEHP concentration in the opposing phase. The variation of K with Z is such that a plot of log K vs. Z, for the trivalent lanthanides, is a straight line of slope 0·4, corresponding to a K_{Z+1} to K_Z ratio of 2·5. The K for Y lies on this line if Y is assigned the artificial Z of 67·6.[4] Although a detailed study of the extraction of Sr(II) and Ba(II) has not been made, the K dependencies are known to be approximately inverse second-power and direct second-power with respect to aqueous acid concentration and HDEHP concentration respectively, in the range of concentrations investigated.

TABLE 1.—K VALUES PERTINENT TO THE ISOLATION OF TRACER-LEVEL ^{90}Sr, ^{140}Ba, ^{90}Y, ^{140}La, ^{144}Ce, ^{143}Pr, AND ^{144}Pr

Solvent composition	Aqueous composition	Element	K
1·5 M HDEHP (toluene)	0·05 M HCl	Sr	6×10^{-2}
		Ba	3×10^{-2}
		Y	$> 10^{5}$
		La	50
1·5 M HDEHP (toluene)	0·1 M HCl	Sr	$1{\cdot}6 \times 10^{-2}$
		Ba	8×10^{-3}
		Y	$> 10^{4}$
		La	6
1·5 M HDEHP (toluene)	0·5 M HCl	Y	$1{\cdot}7 \times 10^{2}$
		La	1×10^{-2}
0·75 M HDEHP (toluene)	5·0 M HCl	Y	$<7 \times 10^{-3}$
		La	$<5 \times 10^{-4}$
0·75 M HDEHP (*n*-heptane)	10 M HNO_3	Ce(IV)	$>8 \times 10^{3}$
		Ce(III)	7×10^{-3}
		La	4×10^{-3}
		Pr	8×10^{-3}
0·30 M HDEHP (*n*-heptane)	10 M HNO_3	Ce(IV)	4×10^{3}
		Ce(III)	1×10^{-3}
		La	3×10^{-4}
		Pr	5×10^{-4}
		Pm	1×10^{-3}
		Eu	5×10^{-3}
		Tm	0·12
0·15 M HDEHP (*n*-heptane)	10 M HNO_3	Ce(IV)	$3{\cdot}3 \times 10^{2}$
		Ce(III)	$< 10^{-4}$

From the foregoing facts, and the data of Table 1, it is apparent that a wide variety of combinations of HDEHP concentration and mineral acid concentration may be used to effect the mutual separation of members of the following combinations: Sr-Y, Ba-La, and La-Y. It is also apparent that these systems show little promise for a Sr-Ba separation. In this connection, it is interesting to note that in each of the two vertical sequences, Sr-Ba and Y-La, the upper element has a K greater than that of the lower.

It follows that fission product ^{90}Sr and/or ^{140} Ba may be separated, by use of the HDEHP–mineral acid system, from all fission product lanthanides. (The system will also rid ^{90}Sr and/or ^{140}Ba of trivalent Pu, Am, and Cm, each of which extracts somewhat better than La.)

It may be noted, from Table 1, that the procedure described in *isolation of* ^{90}Y will not purify ^{90}Y with respect to ^{140}La. Consequently, the procedure is directly applicable to the isolation of high purity ^{90}Y only if an aged ^{90}Sr source material is used. If freshly isolated ^{90}Sr (nearly always containing some ^{140}Ba) is used as a source material, the method may be modified by using 0·5 M HCl in place of 0·1 M HCl. (Table 1.)

Although an aged ^{90}Sr material is to be preferred to a fresh one as a source of ^{90}Y, a fresh ^{140}Ba is to be preferred to an aged one as a source of ^{140}La. For example, a ^{140}Ba material, initially containing the quantity of ^{90}Sr necessary to yield one ^{90}Sr disintegration per thousand ^{140}Ba disintegrations, will, at the end of a 128 day ageing period, contain ^{140}Ba and ^{90}Sr in such a ratio that the two disintegration rates are essentially equal. Consequently, in a ^{140}La product in which ^{140}La and ^{90}Y had been isolated in equal yield 50 per cent of the disintegration rate would be due to ^{90}Y. For this reason in the *isolation of* ^{140}La procedure the ^{90}Y removal step is included (see Table 1). It is apparent that for isolation of ^{140}La from extremely old ^{140}Ba source materials, further ^{90}Y removal steps should be added.

In lanthanide (III) extraction systems involving a concentrated mineral acid, the departures from inverse third-power acid dependency are marked. Consequently, the behaviour of the trivalent lanthanides in a 0·75 M HDEHP (n-heptane)–10 M HNO_3 system can not be predicted from the data of PEPPARD, MASON, MAIER, and DRISCOLL.[4] The data of Table 1 show the feasibility of separating Ce(IV) from all trivalent lanthanides. A high concentration of HNO_3 is used, so that the cerium oxidation may be made at room temperature and rapidly and so that reduction of Ce(IV) to Ce(III) may be held to a minimum in the absence of a large quantity of bromic acid.

In the procedure described in *preparation of cerium for neutron bombardment*, the ratio of Ce(IV) to HDEHP is such that, in the scrubbed extract, the concentration of free HDEHP, i.e., HDEHP not part of the extracting Ce(IV) entity, is considerably less than 0·30 M. (On the assumptions that all of the Ce present in the initial sample is Ce(IV), that all of the Ce(IV) is extracted, and that the ratio of Ce(IV) to (DEHP) in the extracting entity is 1 : 4 the concentration of free HDEHP in the initial extract is approximately 0·02 M.) Consequently, from Table 1, it may be seen that all lanthanide(III) contaminants are readily removable by scrubbing with 10 M HNO_3. It is, therefore, apparent that in the *isolation of* ^{143}Pr *from a neutron-bombarded cerium sample* and the *isolation of* ^{144}Pr *from a* ^{144}Ce–^{144}Pr *source* procedures, the Ce–Pr mutual separation may be made a very efficient one, and is dependent only upon maintaining Ce as Ce(IV).

Although the removal of gross cerium from a 0·75 M HDEHP phase to a 10 M HNO_3 phase containing H_2O_2 as a reducing agent is slow, see *preparation of cerium for neutron bombardment* section, tracer Ce(IV) is reduced by contaminant reducing agents and removed in less than 30 sec from a 0·75 M HDEHP phase to a 10 M NHO_3 phase. Consequently, in order to determine the K for Ce(IV), using trace concentrations of cerium, it is necessary to have a holding oxidant, such as bromic acid, present. In this respect, the behaviour of Ce(IV) parallels that of Bk(IV).[3]

In each of the HDEHP–HNO_3 systems of Table 1, the ratio of the K values of Ce(IV) to that of Ce(III) is seen to exceed 10^6. In the 0·15 M HDEHP–10 M HNO_3 system, the corresponding ratio for the Bk(IV)–Bk(III) pair is approximately 10^6.[3]

In the least-squares analyses for the half-life determinations, data extending over at least eight half-lives were used. For ^{140}La, the data extended over 10 half-lives. The resultant half-lives are presented in Table 2, along with the literature values.

TABLE 2.—NEW HALF-LIFE VALUES FOR ^{90}Y, ^{140}La, ^{143}Pr, AND ^{144}Pr COMPARED WITH LITERATURE VALUES

Nuclide	Half-life		
	Unit	New Value	Literature values
^{90}Y	hours	63·97 ± 0·1	60·5 ± 2·0,[6] 61·0 ± 1·0,[7] 62·0,[8] 64·0,[9] 65·0[10]
^{140}La	hours	40·27 ± 0·05	39·5,[7] 40·0,[8] 40·0 ± 0·1,[12] 40·2,[9] 40·0 ± 0·3,[13] 40·4[14]
^{143}Pr	days	13·59 ± 0·04	13·5 ± 0·1,[15] 13·7 ± 0·1,[16] 13·8,[9][17] 13·95[18]
^{144}Pr	minutes	17·27 ± 0·04	17,[9] 17 ± 2·0,[19] 17·5[20,21]

In extractions involving yttrium or the trivalent lanthanides in gross concentration, the extracting species has been shown to contain none of the original anionic entity of the aqueous feed material, i.e., chloride, nitrate or sulphate, but only the DEHP entity or a variant.[4] From the acid and HDEHP dependencies[4] and the established existence of the dimer, $(HDEHP)_2$,[22] it seems likely that the extracting species is $M[H(DEHP)_2]_2$.

By analogy, Sr(II) and Ba(II) may be assumed to extract as $M[H(DEHP)_2]_2$.

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THE RECOVERY OF THORIUM-230 FROM URANIUM WASTES

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Abstract—A solvent extraction with dibutyl carbitol and tributyl phosphate (TBP) cycles has been used to recover thorium with a ^{230}Th content of 12 per cent from a solid hydroxide waste, containing 6 p.p.m. ^{230}Th, which has arisen from the extraction of uranium from pitchblende. A process consisting of successive counter-current extraction cycles with dilute (5 per cent) and concentrated (40 per cent) TBP which would be of general application to ^{230}Th containing wastes, is outlined.

INTRODUCTION

ORES in which secular equilibrium between uranium and its daughters has been established can be expected to contain ^{230}Th in the ratio ^{230}Th : ^{238}U :: 18 : 10^6. This ratio, which is the ratio of the half-lives, will occur in any ore if there has been no geological separation of thorium from uranium in the ore during the last 2 to 3 million years. In addition, ^{232}Th may be present.

An account of the recovery of gram quantities of ^{230}Th from wastes which have arisen in the processing of Belgian pitchblende for the extraction of uranium has been given by PEPPARD *et al.*[1] The recovery of thorium from such wastes requires the removal of many metals present in macroscopic quantities and an overall volume reduction, so that the thorium is finally obtained in a small bulk of material. To achieve this they used three organic solvents (tributyl phosphate, diethyl ether, and penta-ether) in successive cycles. The extraction of milligram quantities of thorium with a ^{230}Th content of 27 per cent from a Canadian pitchblende residue has also recently been described by VAN CLEAVE and BAERG.[2] The steps used were solvent extraction with mesityl oxide; oxalate and iodate precipitations from nitric acid solution; and a final ion exchange purification.

The existence of ^{230}Th in wastes such as arise either from the recovery of uranium and radium from ores or from the recovery of uranium from sludges after gold extraction is (i) a potential source of a useful tracer for the study of the behaviour of thorium compounds; and (ii) a potential hazard due to the toxicity of ^{230}Th as an α-emitter. Thus at a level of 18 p.p.m. of ^{230}Th in uranium, the recovery of each 1000 tons of uranium leaves 18 kg of ^{230}Th: this is equivalent in α-activity and possibly in toxicity to about 5 kg of plutonium (as ^{239}Pu). Treatment of wastes rich in ^{230}Th may therefore be desirable not merely to recover any associated uranium and to provide a useful isotope, but also to eliminate a health hazard. The method described

* Australian Atomic Energy Commission.

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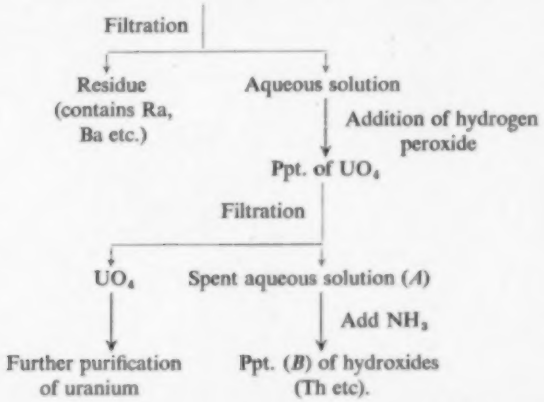
in this paper, by which about 10 g of ^{230}Th have been recovered, differs in certain important respects from earlier methods.

EXPERIMENTAL

Outline of procedure. The early stages in the extraction of uranium from Belgian pitchblende at the Springfields factory of the U.K.A.E.A. have involved the following steps:

Treatment with nitric and sulphuric acids and addition of barium nitrate



The spent aqueous solution (*A*) has contained a small fraction (of the order of 1 per cent) of the total uranium: this fraction has been recovered by the addition of ammonia, to give a precipitate (*B*) which has also contained many other metals present in the ore, including a substantial fraction of the thorium. Both the uranium and thorium have been recovered as nitrates by the following steps:

Step 1. *Uranium recovery.* Preliminary experiments and extractor runs were made on solutions of precipitate (*B*) in order to obtain suitable conditions for operation on a ton scale. The extraction conditions chosen were low nitric acid (~0·5 M) and high total nitrate (3 to 4 M); these were obtained by dissolving the precipitate in a quantity of 12 M nitric acid, sufficient to give the final acidity required. One ton of the precipitate gave approximately 1,200 l. in which the uranium concentration was 5–15 g/l. sulphate was 0·25 M, and the most prevalent metals were aluminium and iron.

Uranium was extracted with an efficiency >95 per cent by counter-current extraction with an equal volume of dibutyl carbitol and one-fifth volume of water as the scrub. The raffinate from this solvent extraction step contained all the thorium present in precipitate (*B*) together with impurities arising from the ore. The major impurities were present in the following typical ratios relative to the thorium: iron 300, aluminium 300, nickel 20. In addition, the following elements were present in amounts comparable to that of thorium: B, Cr, Co, Li, Mn, Si, Sc, Y, Ca, Cd, and Ba.

Step 2. *Volume reduction.* Thorium partition coefficients between the raffinate (~0·4 M HNO_3, ~3 M total nitrate) and various TBP solutions in kerosene were determined for equal volumes of the two phases:

% TBP	20	50	75	100
K_{Th}	0·35	2·1	4·2	7·7

Three successive equal volume extractions with 50 and 100 per cent TBP removed 95 and 99 per cent of the thorium respectively. Stirring with aqueous oxalic acid was examined as a method for the recovery of thorium from the solvent phase. It was shown that with a solvent aqueous ratio of 10 : 1, 88 per cent of the thorium was removed (83 per cent as a precipitate) with a solution of 1 M oxalic acid, and >99 per cent removed (99 per cent as a precipitate) with a slurry of oxalic acid of a total concentration of 2 M.

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Step	Process	Method		Relative volumes	Approx. $^{230}Th + ^{232}Th$ conc.
			Precipitate (*B*)		50 p.p.m.
			↓		
1	Recovery of U	Solvent extraction of U by dibutyl carbitol (or dilute TBP)	Nitric acid solution after filtration	1000	0·05 g/l.
			↓ U extraction		
			Nitric acid raffinate, low in U	1200	0·04 g/l.
			↓		
2	First separation from metal contaminants volume reduction	Solvent extraction of Th by 100% TBP and recovery as oxalate	$Th(NO_3)_4$ in TBP	600	0·05 g/l.
			↓		
			Thorium oxalate slurry	1·5	16 g/l.
			↓		
3	Final separation of metal contaminants	Selective solvent extraction of Th by 40% TBP and recovery as nitrate	Nitric acid solution	6·0	4 g/l.
			↓		
			$Th(NO_3)_4$ in TBP		
			↓		
			$Th(NO_3)_4$ in 0·02M HNO_3	3·5	9 g/l.

A batch process was operated in a stainless-steel plant provided with air filters in the venting lines to avoid contamination of the atmosphere by α- activity. Little emphasis was placed on obtaining a high yield of ^{230}Th, and in practice a 50 per cent yield was achieved by contacting 100 l. of 100 per cent TBP with two successive 100 l. batches of unconditioned raffinate. The thorium in the organic phase was precipitated as oxalate by stirring with 10 l. of 1 M oxalic acid. In this way an aqueous oxalate slurry, in which ^{230}Th was found by α-pulse analysis to be the only α-active constituent, was obtained. Spectrographic analysis showed that thorium, scandium and yttrium were present in

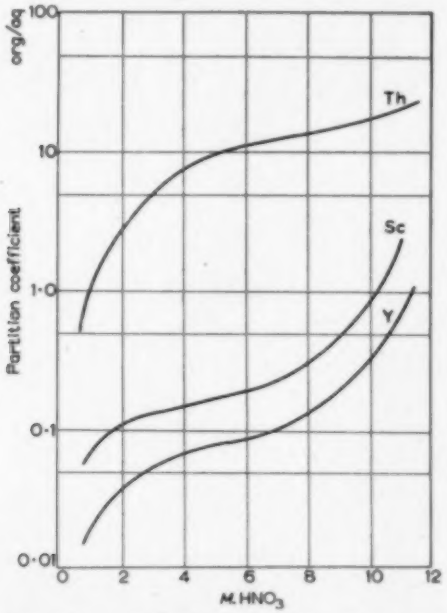

FIG. 1.—Th, Y and Sc partition coefficients between nitric acid and 40 per cent TBP in kerosene.
Th—interpolated values from data in ref. 6.
Y—interpolated values from data in ref. 5.
Sc—constructed assuming Sc/Y ratio for 40 per cent TBP is the same as for 100 per cent TBP (refs. 4 and 5).

approximately equal amounts and that calcium and magnesium were also major components, with iron, lead, cobalt and boron as minor ones.

Step 3. *Final purification.* This was carried out in glass apparatus; owing to the high level (>1 g/l. ^{230}Th) of α-activity in this step, fume hoods were used for initial experiments, e.g. with ~0·1 g ^{230}Th, and more complete protection (a glove box) during the treatment of larger quantities. The oxalate was decomposed by treatment with a cold saturated solution of potassium dichromate in concentrated nitric acid. The final acidity was 6 M. The reaction set in spontaneously after a slight induction period and gave a deep purple solution, due apparently to a chromium complex. 99 per cent of the oxalate could be dissolved in half an hour. Destruction of the oxalate by this method is preferable to the procedure of VOGEL[3] which requires the heating of relatively large quantities of active material with caustic soda solution, followed by the separation and washing of the hydroxide precipitate which is formed thereby.

Thorium and scandium show similar extractability into TBP in the high nitric acid region but the partition of thorium is considerably higher than that of scandium at lower acid concentrations.[4]

[3] A. I. VOGEL, *A Text Book of Qualitative Chemical Analysis* (Third Edition) p. 458. Longmans, Green, London (1948).
[4] D. F. PEPPARD, G. W. MASON, and J. L. MAIER *J. inorg. nucl. Chem.* **3**, 215 (1956)

Yttrium[5] is less readily extracted than scandium. Nitric acid concentrations of 4–6 M are particularly suitable for the separation of these elements with 40 per cent TBP; in this acid range, the plot of the partition coefficient versus acid concentration reaches a plateau in the case of thorium while the partition coefficients for scandium and yttrium are still low (Fig. 1). It is also apparent from Fig. 1 that 3–4 M HNO_3 is suitable for scrubbing the organic extracts to reduce contamination by these two elements. Similar concentrations of sodium nitrate can be used for this purpose; this was tested on a small scale with ^{46}Sc present as a tracer.

Extraction of thorium from the 6 M nitric acid solution was carried out by three successive quarter volume extractions with 40 per cent TBP: the organic phases were combined. The solvent was then scrubbed with a volume of 3 M sodium nitrate equal to one fifth of its volume and backwashed with six successive one third volumes of 0·02 M nitric acid.[6]

Spectrographic analysis of the product showed that scandium was the major impurity (~5 per cent). Small amounts of yttrium were also present; the only other element detected was chromium (<0·1 per cent). Solutions obtained by this procedure are satisfactory for use as a tracer since "weightless" sources are possible.

The ^{230}Th content of the thorium was found by mass spectrographic analysis to be 12·1 per cent ± 0·5 per cent.

Further purification of thorium from scandium was tested by thorium precipitation with phenylarsonic acid.[7] The precipitate, after washing with water, was boiled with 20 per cent caustic soda solution to convert the precipitate to the hydroxide and to remove arsenic. The hydroxide was washed and immediately dissolved in acid. Spectrographic analysis of the product obtained after one precipitation showed scandium (1·5 per cent) and a trace of yttrium; no arsenic was detected.

DISCUSSION

In the process described above, the recovery of uranium was an important consideration: the existence of facilities for handling large volumes of liquor in a counter current extraction system with dibutyl carbitol as the solvent was the determining factor in the selection of the method given for step 1.

On future occasions the choice between (i) a separate uranium removal step prior to thorium extraction and to volume reduction, and (ii) an initial uranium and thorium removal step as adopted by PEPPARD *et al.*,[1] is likely to depend on the scale of operations, plant facilities etc. Although the former procedure involves two solvent extraction cycles, rather than one, each with relatively large volumes of liquor (per gram of ^{230}Th), there are compensating advantages since (a) the α-hazard from ^{230}Th is minimized by the use of dilute solutions up to a later stage of purification, and (b) the same equipment can probably be used for both cycles.

If the recovery of both uranium and thorium is required on a routine basis from wastes of this nature, it would be logical to use 4 to 5 per cent TBP in step 1 and to combine steps 2 and 3 into a single counter-current extraction cycle using 40 per cent TBP. The process would then consist of a two cycle process along the lines suggested by MCKAY and FLETCHER[8] and operated by WELLS and NICHOLLS[9] for the recovery of uranium from irradiated thorium. The partition coefficients for an aqueous feed of the composition used in step 1 are >5 for uranium and ~0·5 for thorium with 5 per cent TBP. For the thorium recovery cycle, a counter-current process with

[5] D. SCARGILL, K. ALCOCK, J. M. FLETCHER, E. HESFORD, and H. A. C. MCKAY *J. inorg. nucl. Chem.* **4**, 304 (1957).
[6] E. HESFORD H. A. C. MCKAY, and D. SCARGILL *J. inorg. nucl. Chem.* **4**, 321 (1957).
[7] W. W. SCOTT and N. H. FURMAN *Standard Methods of Chemical Analysis* (Fifth Edition) Vol. 1, p. 952. Technical Press, London (1952).
[8] H. A. C. MCKAY and J. M. FLETCHER *Progress in Nuclear Energy* Ser. III, *Process Chemistry* Vol. 1, p. 147. Pergamon Press, London (1956).
[9] I. WELLS and C. M. NICHOLLS *Progress in Nuclear Energy* Ser. III, *Process Chemistry* Vol. 1, p. 223. Pergamon Press, London (1956).

40 per cent TBP could effectively remove all metal contaminants, giving a high thorium recovery and a ^{230}Th-free raffinate.

Acknowledgements—The development of steps 1 and 2 was carried out by the Research and Development Branch of the U.K. Atomic Energy Authority at Springfields and Windscale: we are grateful to Mr. J. A. DUKES, Dr. A. AUDSLEY and Mr. C. H. FAZAKERLEY of the former and to Messrs. G. E. EASTWOOD, H. W. MATTHEWS and A. P. PREECE of the latter for the information made available. We are also indebted to Mrs. D. WILLIAMS and Mr. F. T. BIRKS, who carried out the spectrographic analyses, and to Dr. G. R. HALL and Mr. A. J. WALTER for the mass spectrographic determination.

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ANNOUNCEMENT

Dr. Manning has kindly undertaken to serve as Acting American Editor in the absence of Dr. J. J. Katz, who is on sabbatical leave in Cambridge. England, until mid-1958.

Communications which would normally be sent to Dr. Katz can, therefore, be sent to Dr. W. Manning, Argonne National Laboratory, Box 299, Lemont, Illinois, U.S.A.

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 153 to 158. Pergamon Press Ltd., London

THE OCCURRENCE OF MOLYBDENUM-99 IN NATURAL AND IN DEPLETED URANIUM SALTS AND THE SPONTANEOUS FISSION HALF-LIFE OF URANIUM-238*†

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(*Received* 23 *May* 1957)

Abstract—Measurements of the $^{99}Mo/^{238}U$ equilibrium ratios in aqueous solutions of non-irradiated uranium salts gave the following results: $(4{\cdot}4 \pm 0{\cdot}4) \times 10^{-4}$ and $(4{\cdot}4 \pm 0{\cdot}3) \times 10^{-4}$ disintegrations per second of ^{99}Mo per gramme of ^{238}U in natural uranium and in depleted uranium, respectively. A value of $(8{\cdot}0 \pm 0{\cdot}5) \times 10^{15}$ years, which agrees with Segrè's value, is obtained from the above data for the spontaneous fission half-life of ^{238}U, if one assumes that the yield of ^{99}Mo is 6·4 per cent and the spontaneous fission of ^{238}U is the only source of ^{99}Mo.

IT HAS recently been reported by the authors[1] that ^{99}Mo (half-life 67 hr) occurs in non-irradiated natural uranium salts at an extremely low, but measurable, concentration.

Studies on the natural occurrence of ^{99}Mo are of a special interest, since it decays into ^{99}Tc (half-life $2{\cdot}1 \times 10^5$ years), of which the terrestrial occurrence has not yet been established.

Aside from the nuclear-geochemical interest, the present study was undertaken by the authors with the following objects in mind: (a) to obtain, radiochemically, a more accurate value of the spontaneous fission rate of ^{238}U, (b) to determine the yield of ^{99}Mo in spontaneous fission of ^{238}U, and (c) to estimate the contribution of the neutron-induced fission of ^{235}U in natural uranium bearing materials.

The equilibrium ratios of $^{99}Mo/^{238}U$ in depleted uranium, as well as in natural uranium, have been determined. The amounts of ^{99}Mo found in the uranium salts agreed with the calculated value from the spontaneous fission half-life of ^{238}U, reported by SEGRÈ,[2] thus indicating that the ^{99}Mo is formed mainly by the spontaneous fission of ^{238}U.

EXPERIMENTAL

Materials

Natural uranium. Commercial uranyl nitrate (Mallinckrodt reagent grade) was used in the experiments on natural uranium. The $^{238}U/^{235}U$ ratio was not measured, but was assumed to be that of natural uranium. A large stock solution was made by dissolving 3,420 g of the salt in 10 l. of dilute nitric acid. Molybdenum carrier was added to the solution and then removed by precipitation of the Mo-α-benzoinoxime complex as described in the following paragraphs. The molybdenum precipitate was discarded. The uranium solution was then stored for at least 3 weeks, until equilibrium between ^{99}Mo and ^{238}U was re-established.

* This paper represents a part of the dissertation submitted by P. L. PARKER to the Graduate School of the University of Arkansas in partial fulfilment of the requirement for the degree of Master of Science.

† Presented at the Southwide Chemical Conference, 6 December 1956, Memphis, Tennessee.

(1) P. L. PARKER and P. K. KURODA *J. chem. Phys.* **25**, 1084 (1956).

(2) E. SEGRÈ *Phys. Rev.* **86**, 21 (1952).

Depleted uranium (99·989 *per cent* ^{238}U, 0·011 *per cent* ^{235}U). The depleted uranium was made available to us by Dr. H. M. ROTH of the Research and Development Division, U.S.A.E.C., Oak Ridge, Tennessee. The uranium was obtained as the oxide. A large stock solution was prepared by dissolving the oxide in a minimum amount of concentrated nitric acid. An insoluble residue was removed by filtration. Molybdenum carrier was added and removed, and the solution stored until equilibrium was re-established. The uranium concentration of this stock solution was determined by gravimetric analysis to be 225·3 g U per l.

Molybdenum carrier. A carrier solution of molybdenum was prepared by dissolving 1·8461 g of ammonium molybdate in 1 l. of distilled water.

Lead acetate buffer solution. A buffer solution of lead acetate was prepared as described by STERLING and SPUHR.[3]

Other solutions. Fisher α-benzoinoxime was used to prepare a roughly 2 per cent solution in ethanol. All other chemicals were reagent grade. Extreme care was taken to avoid contamination of the reagents. All solutions were prepared in new glassware.

Procedure for the separation and purification of molybdenum

The chemical procedure used in this study is a synthesis of several known procedures. The same procedure was followed for both the natural and the depleted uranium. The procedure will be best presented in the form of an outline of a particular experiment which was performed.

A volume of solution (about 5 l.) containing 1190 ± 10 g of uranium (5 moles) was taken from the previously prepared stock solution. To this solution 50 mg of molybdenum carrier and few ml of bromine water were added. A 100 ml portion of the α-benzoinoxime solution was then added slowly with stirring.[4] The fluffy, white precipitate of the α-benzoinoxime-molybdenum complex began to form at once. The uranium solution had been cooled overnight to aid precipitation. The precipitate was filtered, washed with 0·01 M nitric acid and transferred into a 250 ml beaker. To the beaker containing the precipitate 10 ml each of hydrogen peroxide (30 per cent) and ammonia were added. The precipitate dissolved when this solution was warmed until no more oxygen was evolved. Iron scavenger (10 mg) was added to this basic solution and the ferric hydroxide which formed was removed by filtration. The clear solution was then cooled (10°C) and acidified with nitric acid. Molybdenum was again precipitated by the addition of α-benzoinoxime. This process of precipitation, dissolution and scavenging was repeated seven times.

After the seventh iron scavenging step the basic solution was shaken with 50 ml of chloroform containing a little dithiozone in a separating funnel, and the chloroform layer was discarded. The aqueous phase was made 6 N in hydrochloric acid, and was shaken with three 50 ml portions of methyl-*iso*butyl-ketone in a separating funnel.[5] Molybdenum was extracted into the organic layer, and the aqueous layer was discarded. The organic layer was shaken with two 50 ml portions of distilled water. The molybdenum was extracted back into the aqueous layer. The aqueous layer was added to 100 ml of a hot lead acetate buffer solution. Lead molybdate

[3] C. STERLING and W. P. SPUHR *Ind. Engng Chem.* (*Anal.*) **12**, 33 (1940).
[4] N. E. BALLOU *Radiochemical Studies: The Fission Products* Div. IV. Book 3, p. 1538. National Nuclear Energy Series (1951).
[5] I. NELIDOW *J. phys. Chem* **59**, 710 (1955).

was precipitated, collected by filtration, dried, and mounted on aluminium for counting. The chemical yield was usually about 60 per cent. New glassware was used in the last half of the procedure.

Counting equipment

A pancake-type Gieger-Müller counter (Anton 1007 TA, 2 mg cm^{-2} mica window), which had a background of $1{\cdot}05 \pm 0{\cdot}05$ counts/min in anti-coincidence with the surrounding counters, was used for the radioactivity measurements.

The counter used was calibrated using a standard sample of chlorine-36 prepared and calibrated by Prof. ROBINSON of the Department of Physics, by the 4π counting

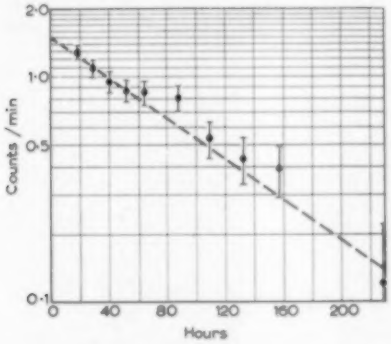

FIG. 1.—Observed decay of ^{99}Mo.

method.[6] The effect of the self-absorption was checked by counting various beta-active isotopes in various amounts of carriers.

Determination of slight activity in reagents

To check the reagents, 50 mg of molybdenum carrier was precipitated with an excess of lead acetate buffer solution. The precipitate was filtered, dried, and counted. The activity was found to be $0{\cdot}18 \pm 0{\cdot}03$ counts/min per 192·3 mg $PbMoO_4$ and it remained essentially constant for several days. No effort was made to purify the lead or molybdate reagents used.

This slight activity from lead molybdate was observed in all the experiments described later as a "tail" of the decay curve of ^{99}Mo, thus making the observed half-lives of ^{99}Mo somewhat longer than the theoretical 67 hr. When this activity was subtracted from the observed decay curves, decay curves with a half-life of 70 ± 10 hr were obtained.

RESULTS AND DISCUSSION

^{99}Mo in natural uranium

The natural uranium solution used contained 1,182 g of ^{238}U (8 g of ^{235}U). Molybdenum carrier (50 mg) was added and lead molybdate was recovered as described in the chemical procedure. The chemical yield was 81 per cent (156·4 mg $PbMoO_4$). The correction for the activity of the carrier was 0·15 counts/min. The background

[6] P. K. KURODA, R. R. EDWARDS, B. L. ROBINSON, J. H. JONTE and C. GOOLSBY *Geochim. et Cosmoch. Acta* **11**, 194 (1957).

of the counter was 1·05 ± 0·05 counts/min. The counting results are presented in Table 1 (experiment I) and also in Fig. 1.

In a second experiment the natural uranium solution used contained 1,610 g of ^{238}U (11 g of ^{235}U). Molybdenum carrier (50 mg) was added and lead molybdate was

TABLE 1.—DECAY OF ^{99}Mo ISOLATED FROM NATURAL URANIUM

Experiment I		Experiment II	
Time after initial Mo separation (hr)	^{99}Mo activity (counts/min)*	Time after initial Mo separation (hr)	^{99}Mo activity (counts/min)*
0	1·5 ± 0·1 (I_0)†	0	1·6 ± 0·1 (I_0)†
18	1·29	17	1·35
29	1·09	30	1·26
41	0·95	43	1·05
52	0·87	54	0·86
65	0·85	65	0·76
88	0·80	77	0·79
108	0·53	89	0·72
133	0·43	101	0·61
157	0·39	119	0·55
228	0·12	149	0·40
		170	0·32
		175	0·32
		184	0·31

* ^{99}Mo activity is the observed activity, less the background, less the correction for the carrier activity.

† I_0 is the ^{99}Mo activity at the time of the initial separation, obtained graphically.

recovered according to the procedure described earlier. The chemical yield was 46·3 per cent (89 mg of $PbMoO_4$). The correction for the carrier activity was 0·08 counts/min. and the background was 1·05 ± 0·05 counts/min. The counting results are shown in Table 1 (experiment II).

^{99}Mo *in depleted uranium*

The depleted uranium solution used contained 1,275 g of uranium (0·14 g of ^{235}U). Molybdenum carrier (40 mg) was added and lead molybdate was recovered according to the procedure described earlier. The chemical yield was 55·4 per cent (82·2 mg $PbMoO_4$). The correction for the activity of the carrier was 0·08 counts/min. The background of the counter was 1·15 ± 0·05 counts/min. The counting results are presented in Table 2 (experiment III).

In a second experiment the depleted uranium solution used contained 1,275 g of uranium (0·14 g of ^{235}U). Molybdenum carrier (40 mg) was added and lead molybdate was recovered in the usual way. The chemical yield was 63·7 per cent (98·4 mg $PbMoO_4$). The correction for the activity of the carrier was 0·09 counts/min. The

background of the counter was $1{\cdot}05 \pm 0{\cdot}05$ counts/min. The counting results are presented in Table 2 (experiment IV).

TABLE 2.—DECAY OF ^{99}Mo ISOLATED FROM DEPLETED URANIUM

Experiment III		Experiment IV	
Time after initial Mo separation (hr)	^{99}Mo activity (counts/min)*	Time after initial Mo separation (hr)	^{99}Mo activity (counts/min)*
0	$1{\cdot}5 \pm 0{\cdot}1$ (I_0)†	0	$1{\cdot}5 \pm 0{\cdot}1$ (I_0)†
22	1·22	17	1·25
38	1·03	28	1·02
59	0·97	41	1·01
71	0·74	53	0·86
84	0·77	65	0·91
91	0·67	86	0·76
113	0·65	111	0·57
137	0·44	135	0·48
159	0·34	160	0·31
183	0·23		
391	0·14		

* ^{99}Mo activity is the observed activity, less the background, less the correction for the carrier activity.

† I_0 is the ^{99}Mo activity at the time of the initial separation, obtained graphically.

The ^{99}Mo/^{238}U equilibrium ratio in uranium salts

The ^{99}Mo/^{238}U equilibrium ratios in aqueous solutions of natural and depleted uranium were calculated from the counting data shown in Tables 1 and 2, and the results are summarized in Table 3.

TABLE 3.—THE ^{99}Mo/^{238}U EQUILIBRIUM RATIO IN URANIUM SOLUTION

	Natural uranium	Depleted uranium
Disintegrations per sec per g ^{238}U	$(4{\cdot}4 \pm 0{\cdot}4) \times 10^{-4}$	$(4{\cdot}4 \pm 0{\cdot}3) \times 10^{-4}$

The ^{99}Mo/^{238}U equilibrium ratio in natural uranium agrees, within the experimental error, with that in depleted uranium.

If one assumes that the spontaneous fission of ^{238}U is the only source of ^{99}Mo,

$$^{99}\text{Mo (d/sec)}/^{238}\text{U (d/sec)} = T_{1/2\alpha}/T_{1/2f} \cdot y \qquad (1),$$

where $T_{1/2\alpha}$ is the half-life of ^{238}U for alpha decay, $T_{1/2f}$ is the half-life of ^{238}U for spontaneous fission and y is the spontaneous fission yield of ^{99}Mo.

Substituting the observed $^{99}Mo/^{238}U$ ratio, $T_{1/2x} = 4{\cdot}51 \times 10^9$ years, and $T_{1/2f} = 8{\cdot}04 \times 10^{15}$ years,[2] into equation (1), one obtains a value of $y = 0{\cdot}064 \pm 0{\cdot}005$ for the spontaneous fission yield of ^{99}Mo, or if one assumes that the yield of ^{99}Mo is 6·4 per cent, a value of $(8{\cdot}0 \pm 0{\cdot}5) \times 10^{15}$ years, which agrees with SEGRÈ's value, is obtained for the spontaneous fission half-life of ^{238}U.

If one takes PERFILOV's value,[7] $(1{\cdot}3 \pm 0{\cdot}2) \times 10^{16}$ years, for the spontaneous fission half-life of ^{238}U, to be correct, the observed $^{99}Mo/^{238}U$ ratio gives a value of $y = 10$ per cent.

The exact shape of the yield-mass curve has to be determined by measurements of the equilibrium ratios of various other fission products to uranium in non-irradiated uranium salts, before a correct value of y can be assigned to ^{99}Mo. Experiments along this line are now being carried out in this laboratory.

The fact that no significant difference was observed between the $^{99}Mo/^{238}U$ equilibrium ratios in natural and in depleted uranium is probably due to the small values of the effective multiplication constant, k_{eff}, of the uranium solutions used in the experiments, as pointed out by ASHIAZWA and KURODA,[8] who found no significant difference between the short-lived iodine isotopes/^{238}U equilibrium ratios in natural and in depleted uranium salts.

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Acknowledgements—This investigation was made possible by support from the U.S. Atomic Energy Commission. Special thanks are due to Dr. H. M. ROTH of the Research and Development Division, U.S. Atomic Energy Commission, Oak Ridge, Tennessee, for furnishing the depleted uranium sample used in this study. We are also grateful to Prof. B. L. ROBINSON of the Western Reserve University for his valuable advice.

[7] N. A. PERFILOV *J. exp. theor. Phys.* **17**, 476 (1947); *Chem. Abstr.* **42**, 2864 (1948).
[8] F. T. ASHIZAWA and P. K. KURODA *J. inorg. nucl. Chem.* In press.

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 159 to 160. Pergamon Press Ltd., London

SZILARD-CHALMERS REACTIONS AND RELATED PROCESSES IN OXIDES—I

CHEMICAL STATE OF ^{239}U IN NEUTRON-IRRADIATED U_3O_8

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(*Received* 25 *February* 1957)

Abstract—Tetravalent and hexavalent uranium isolated from U_3O_8 irradiated with slow neutrons, were found to have the same specific activity of ^{239}U.

DISCUSSION

THE data available concerning Szilard-Chalmers reactions and similar phenomena in solid salts like chlorates or phosphates suggest that it would be of interest to study corresponding processes in a simpler class of compounds, the oxides. U_3O_8 seemed to offer an attractive possibility.

Two different mechanisms may be suggested for Szilard-Chalmers effects in oxides:

(1) First of all it might happen that the lattice which has been disturbed locally by the recoil of the activated nucleus does not return to its original structure but adopts a different configuration, which is sufficiently stable to last for a reasonable period of time at room temperature. In this abnormal region the radioactive atom may be present as a different type of ion. In principle a process of this kind can be imagined for any oxide containing an element that may have different valencies. We may add here that to us this mechanism seems the most likely one to be realized.

(2) An entirely different possibility exists in lattices which contain cations of the same element but in more than one valency state. Here we must recognise two different types, those crystals in which one can distinguish between the positions occupied by cations of one valency and those of the other valency, and crystals in which the positions of the cations of the two valencies are identical. (There are arguments to suggest that U_3O_8 belongs to the latter[1] group.) In a lattice of the first mentioned type it might be possible that, as the lattice returns to its original structure, radioactive atoms would move preferentially to one or the other kind of position, and in this way a Szilard-Chalmers separation might be possible. In solids of the second group one does not see how a separation of this type could take place and for these oxides it seems reasonable to consider only mechanism (1).

We found ^{239}U distributed equally over the U^{4+} and U^{6+} ions, or, in other words, the specific activity of both uranium fractions was found equal to within a few per cent. This result suggests that after the oxide lattice has been disturbed by a recoil process the main part of the disturbed region assumes again its original structure. This in contrast to the behaviour normally observed in solids consisting of more than two elements like phosphates, iodates and the like.

[1] F. GRØNVOLD. *Nature, Lond.* **162,** 70 (1948).

It remains to be discussed whether our results can have been influenced by ionization damage in the crystal, a suggestion which might possibly be made because of the occurrence of fission in our samples in view of the high energy involved in the fission process. The number of atoms of ^{239}U formed in our preparation is of the order of 10^8 per g. The number of the fission processes is of the same order of magnitude, which indicates that the total energy liberated per g must have been of the order of 10^{16} or 10^{17} eV/g, far too small to cause appreciable damage to the crystal lattice.

EXPERIMENTAL

U_3O_8 was irradiated with neutrons produced by bombarding beryllium with 26 MeV deutrons in the Philips synchroclotron. The neutrons were slowed down in paraffin.

After irradiation the U_3O_8 was treated with 40 per cent HF to dissolve the hexavalent uranium as UO_2F_2 and precipitate the uranous fraction as UF_4. The UF_4 was dissolved in nitric acid and boric acid and each fraction was purified by ether extraction from a solution containing ammonium nitrate. After back-extraction into water uranium was precipitated with ammonium hydroxide and calcined to form U_3O_8 which was measured under a Geiger counter. Equal weights of both fractions were taken to avoid corrections for self-absorption. When we used this technique differences were found between the specific activities of the two fractions which varied around 5–10 per cent. In our best experiments we added an excess of ammonium carbonate after the back-extraction and added ferric ions to obtain a scavenging precipitate, which was filtered off. After this we boiled with an excess of nitric acid before ammonium uranate was precipitated. In this way the differences in specific activity between the two fractions were reduced to about one per cent (spec. act. U^{4+}/spec. act. $U^{6+} = 1{\cdot}00$; 0·99, and 1·00).

To find out whether exchange between ions in solution and ions of the solid takes place during the process of dissolution we dissolved irradiated U_3O_8 in HF and water containing an excess of inactive uranyl nitrate, roughly equivalent to the amount of uranium present in the oxide. The ratio of the observed specific activities agreed with that calculated from the assumption that no exchange takes place to within 2 per cent.

A complication occurs in this work due to the presence of UX_{II}. (All measurements were done with an absorber of 27 mg aluminium per cm² in front of the counter window, in order to render negligible the counting of UX_I.) For all experiments U_3O_8 was freshly purified by extraction into ether and back extraction into water to reduce as far as possible the counting rate due to UX_{II} in equilibrium with UX_I.

We always measured the growth of the UX_{II} activity in our sample and in some cases the back extrapolated value when subtracted from the rest of the activity provided a clear decay curve with the correct half-life of ^{239}U, i.e. 23·5 min. In our best experiments, however, this method for breaking down the curves did not prove sufficiently accurate (owing partly to the ^{239}Np grown into the samples, but also partly to some unknown impurity). In these cases we analysed our curves by assuming a 23·5 min period and a very long one of suitable intensity.

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SZILARD-CHALMERS REACTIONS AND RELATED PROCESSES IN OXIDES—II

CHEMICAL STATE OF METASTABLE ^{204}Pb IN NEUTRON-IRRADIATED Pb_3O_4

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(*Received* 25 *February* 1957)

Abstract—After irradiation of Pb_3O_4 with fast neutrons, the specific activity of ^{204m}Pb was found to be the same in the plumbous and in the plumbic fraction.

DISCUSSION

AFTER it had been established that in neutron-irradiated U_3O_8 the specific activity of ^{239}U is the same in the U^{4+} and the U^{6+} fractions, it seemed interesting to perform a similar investigation with a solid in which—contrary to the situation which seems to exist in U_3O_8[1]—the cations of the two different valencies occupy places in the lattice which are clearly different. For this type Pb_3O_4 seemed to offer a good example, as the lattice contains rows of plumbic ions and rows of plumbous ions.[2]

By far the most noticeable activity in lead after irradiation with neutrons is the 68 min period of ^{204m}Pb. This is, of course, obtained only with neutrons of high energy. This means that after activation the ^{204m}Pb nucleus has a much higher energy than a nucleus activated by neutron-capture. Although it is well known that this difference in energy may influence the ratio of the specific activities of different chemical fractions,[3] we are inclined to think that this difference is of a quantitative nature only. As it was our main concern to know whether any difference in the specific activity would occur at all between the Pb^{2+}, and the Pb^{4+} fractions, we felt that the product of the *n*,*n*-reaction would serve our purpose satisfactorily.

Within the accuracy of our measurements we found the concentration of ^{204m}Pb to be the same in the lead of the Pb^{2+} fraction and that of the Pb^{4+} fraction. This may be taken to support the conclusion reached in the preceding paper of this series[4] that among oxides cases occur where (in contrast to the behaviour in many of the more complicated crystals), after a nuclear activation process the main part of the disturbed lattice resumes its original structure. The possibility discussed in the preceding paper that in an oxide, in which all cations do not occupy equivalent

[1] F. GRØNVOLD *Nature, Lond.* **162**, 70 (1948).
[2] S. T. GROSS *J. Amer. chem. Soc.* **65**, 1107 (1943).
[3] R. H. SCHULER and C. E. MCGAULEY *J. chem. Phys.* **25**, 1080 (1956).
[4] A. H. W. ATEN, JR., MARIA J. BEERS and D. C. DE GROOT, *J. inorg. nucl. Chem.* **5**, 159 (1957).

positions, the activated nucleus might go to one of the types of cation sites by preference, is not supported by our observations. Anyway, this possibility seems—*a priori*—unlikely to be realised, as it must be much easier to readjust the electrical charge of a cation in the lattice than to move it from one site to another.

It might be asked whether the intensity of the neutron irradiation could cause sufficient damage to the crystal lattice to influence our result. It can be estimated that the number of neutrons which have passed through 1 cm^2 during the irradiation at the position of the sample is of the order of 10^{13}. It is quite evident that only an extremely small fraction of the cations in the lattice can have been displaced by this treatment. The influence of the γ-rays is more difficult to estimate, but in general this radiation has little influence on the structure of a crystal.

EXPERIMENTAL

^{204m}Pb was formed by irradiation with fast neutrons obtained by bombarding beryllium with 26 MeV deuterons in the Philips synchrocyclotron. Gamma-rays only were measured and we used thin-window Geiger counters with absorbers of 1200 mg aluminium per cm^2 to cut out β-rays and other electrons. In no case did we observe other periods than that of 68 min, but our activities were generally low. Statistical errors may well have been the limiting factor in the accuracy of our experiments.

The only satisfactory way of separating plumbous and plumbic ions which we have found was the method given by ZINTL and RAUCH.[5] This involves the precipitation of barium plumbate in a concentrated solution of KOH.

Experiments with ThB indicated that satisfactory results can be obtained in this way if a reprecipitation step is included. If, however, Pb_3O_4 was dissolved in an alkaline plumbite solution a partial exchange between the Pb^{2+} and the Pb^{4+} was observed. This complication was reduced to a negligible one by dissolving the Pb_3O_4 in concentrated acetic acid. (In the experiments with ThB and concentrated acetic acid an active deposit on platinum was dissolved in the acid as a first step and we were unable in these cases to use a reducing agent to make sure that all of the ThB was in the plumbous state before the Pb_3O_4 was dissolved. Even so our two experiments gave specific activities in the Pb^{4+} fraction which amounted to between 4 and 5 per cent of those in the Pb^{2+} fraction. We are, at present, unable to say whether this small contamination is due to exchange, to shortcomings of our analytical method or to the fact that a few per cent of the ThB dissolves as plumbic ions.)

The separation was performed as follows. Pb_3O_4 is dissolved in glacial acetic acid. This liquid is poured into 12 M KOH with very vigorous stirring. The precipitation of PbO_2 which occurs at this stage must remain negligible, as its formation is known to cause exchange.[6] For this reason the lead concentration must be kept low. Barium hydroxide is added, the solution is boiled for some minutes and the mixture of Ba_2PbO_4, $BaCO_3$ and $Ba(OH)_2$ is filtered off on a glass filter. From the filtrate—in which the absence of Pb^{4+} is demonstrated by a test with HCl, KI and starch—the plumbous fraction is isolated as the sulphide, which is converted to $PbSO_4$ by treatment with nitric acid, evaporating to near dryness, washing with a mixture of alcohol and sulphuric acid followed by pure alcohol and finally drying at 120°.

The precipitate which contains the barium plumbate is treated with a solution of K_2CO_3. This brings the plumbate back into solution and it is reprecipitated with $Ba(OH)_2$. The lead from the barium plumbate is again brought into solution by means of a K_2CO_3 solution and the plumbic fraction converted to $PbSO_4$ as described above. The yield of the Pb^{4+} fraction is always much lower than that of the Pb^{2+} fraction.

In three experiments we obtained for the ratio of the specific activities of Pb^{4+} and Pb^{2+}, the values 1·03, 1·02, and 1·08; the true value is probably equal to unity within the accuracy of our experiments.

It remains to be discussed whether an accidental reduction of plumbic ions might have taken

[5] E. ZINTL and A. RAUCH *Ber. dtsch. chem. Ges.* **57**, 1739 (1924).
[6] E. A. E. EVANS, J. L. HUSTON and T. H. NORRIS *J. Amer. chem. Soc.* **74**, 4985 (1952).

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place during the chemical treatment, a possibility suggested by the low yield obtained for this fraction. It is evident that such a reduction does not affect our results at all if it takes place after the first precipitation of barium plumbate. If it should take place before this precipitation it would decrease the difference between the specific activities of the two fractions, but it would not make them equal, if they had not been so originally in the Pb_3O_4. However, the negative result of the iodide test makes it seem unlikely that a reduction has occurred at all during the first stage of the separation.

Acknowledgements—We have pleasure in thanking the crew of the Philips synchrocyclotron for a number of irradiations.

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THE REACTIONS OF TRITIUM TRAPPED IN INORGANIC CRYSTALS*

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(*Received* 26 *April* 1957)

Abstract—Tritium produced and trapped in neutron irradiated LiCl has been released by solution under a variety of conditions. With acetone as the solvent, a variable fraction of the activity reaches stable chemical combination in tritium-labelled acetone. A large amount of activity is found as labile hydrogen after solution in acetone, ethyl alcohol, and acetic acid. The acetone results indicate the presence of a reactive species of hydrogen in the irradiated LiCl.

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LARGE numbers of tritium atoms may be produced in inorganic lithium salts by the $^6Li(n,\alpha)^3H$ nuclear reaction. These tritons travel about 40 μ through the crystal before stopping, producing a nearly uniform distribution of tritium trapped throughout the inorganic lattice. When this lattice is subsequently destroyed by solution of the salt in an appropriate solvent, this tritium, if not already in stable chemical combination, is freed to react with those molecules present in the solution.

Since these reactions may in part be the reactions of free hydrogen atoms or ions in condensed media, they are of interest because they represent an extension of the known chemical reactions of atomic hydrogen into liquid and solid media. The detailed analysis of reaction yields under various conditions may also furnish useful information about the inorganic crystal itself.

EXPERIMENTAL

Irradiations

Three separate irradiations of LiCl were carried out at −196°C. Each irradiation consisted of 20–25 pellets in an aluminium tube, each pellet containing approximately 50 mg LiCl powder wrapped in aluminium foil. Prior to wrapping, the LiCl was dried for 5 hr at 140° in a vacuum oven. The irradiations were carried out in the liquid-nitrogen facility of the Brookhaven National Laboratory reactor for a period of 24 hr each (flux = $4{\cdot}0 \times 10^{12}$ n/cm² sec). After irradiation, the aluminium tubes were stored under the liquid nitrogen until use.

Experiments were performed by adding one or more pellets to a solution at a controlled temperature. The pellets were opened with a stirring rod, the powder dispersed, and the solution stirred. In many cases, the LiCl was only slowly soluble with visible residues over a period of 24–72 hr. Initially, the irradiated powder was black from radiation damage, but the residues often changed colour from black to white, while gradually diminishing in total amount. The colour change did not represent complete solution and reformation of the crystals, however, for filtration

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of white residues and subsequent counting invariably showed large amounts of tritium activity still remaining in the residue. The size and characteristics of the residues are an important source of the variations in specific activity found in different solutions. The process of solution was much faster (no residues remained after an hour or two) in samples which contained water, ethyl alcohol, or acetic acid.

TABLE 1.—TRITIUM LABELLED ACETONE PRODUCED BY SOLUTION IN ACETONE OF LiCl IRRADIATED AT −196°C WITH THERMAL NEUTRONS

Irradiation number	Temperature solution (°C)	Tritium in 2,4-DNPH of acetone (d.p.m./mg)	Tritium in solution (d.p.m./mg)
1	30	4600	215,000
	30 (to 56 briefly)	56,000	275,000
2	−78	100	200,000
	0	85	108,000
	30	350	175,000
	30	200	175,000
	30	230	150,000
	30	150	150,000
	30	170	46,000
	30	600*	98,000*
	50	1500	140,000
3	−78	65	41,000
	30	610	60,000
	30	1910	87,000
	45	140	21,000
Exchange in derivative formation		20	430,000

* Dissolved in absence of air.

Preliminary irradiations were carried out with both LiCl and $LiNO_3$ at room temperature. These samples dissolved with noticeable evolution of gas, at least in part from the trapped helium also produced by the $^6Li(n,\alpha)^3H$ reaction.

Chemical

Carbon-bound tritium activity was differentiated from labile hydrogen through the formation of standard derivatives:

Acetone. 1 ml of solution added to 100 ml of a saturated solution of 2,4-dinitrophenylhydrazine in 2 N HCl at room temperature. After 2 hr, the precipitate was filtered and then recrystallized from ethyl alcohol.

Acetic acid. 2 ml of acid was added to 5 ml H_2O, and neutralized with 5 per cent

NaOH. A hot solution of 1 g benzylisothiourea HCl in 95 per cent ethanol was added to the test solution, and the mixture placed in an ice bath for 45 min. The precipitate was recrystallized from water and ethyl alcohol.

Ethyl alcohol. 1 ml of ethyl alcohol was distilled from its solution in 500 ml H_2O,

TABLE 2.—TRITIUM-LABELLED ACETONE PRODUCED BY SOLUTION OF THERMAL NEUTRON IRRADIATED LiCl (−196°C) IN VARIOUS SOLUTIONS AT 30°C

Irradiation number	Solvent (volume %; remainder acetone)	Tritium in 2,4-DNPH of acetone (d.p.m./mg)	Tritium in solution (d.p.m./mg)
1	10% EtOH	300	215,000
	20% EtOH	270	225,000
	50% EtOH	375	265,000
	DPPH (1·3 mg in 10 ml)*	630	195,000
	50% Diphenyl ether	2500	—
	50% Anethole	1900	—
3	1% EtOH	470	—
	3% EtOH	25	47,000
	5% EtOH	20	—
	7% EtOH	80	—
	10% EtOH	70	56,000
	2% H_2O	60	—
	3% H_2O	20	—

* Diphenyl picryl hydrazyl.
— Not measured.

in order to reduce the concentration of labile tritium activity. A precipitate was then formed by addition of the alcohol to 3·5 dinitrobenzoyl chloride, washed with 2 per cent Na_2CO_3, and recrystallized from ethanol–water solutions.

Total tritium content of the solutions was usually measured, as well as the activity of residues when they occurred. Fractional distillation of some of the mixtures of the acetone solutions with water showed that the bulk of the tritium activity in these solutions was exchangeable with added —OH groups. The tritium activity was measured by gas proportional counting of the gas mixture from zinc fusion.[1]

Exchange reactions

Exchange of labile hydrogen during the formation of derivatives occurs with many derivatives ordinarily used in the identification of ethyl alcohol, acetic acid, and acetone. However, with the methods listed above, derivative formation in the presence of labile tritium and inactive solvent showed very little tritium activity in the precipitates. These results are included for comparison in the tables of solution experiments.

[1] K. WILZBACH, L. KAPLAN and W. G. BROWN *Science* **118**, 522 (1953).

Tritium radioactivity can also be introduced into acetone by the slow exchange of labile hydrogen through the keto-enol mechanism. Previous investigations have shown this exchange to be slow in neutral solution and much more rapid in the presence

TABLE 3.—TRITIUM-LABELLED SOLVENT PRODUCED BY SOLUTION AT 30°C OF LiCl IRRADIATED AT −196°C WITH THERMAL NEUTRONS

Irradiation number	Solvent	Tritium in derivative (d.p.m./mg)	Tritium in solution (d.p.m./mg)
1	Ethyl alcohol	30	2×10^5
	Exchange reaction	30	3×10^5
1	Acetic acid	80–100	2×10^5
	Exchange reaction	60–80	$2{\cdot}5 \times 10^5$

of either acid or base.[2] Under the conditions of these experiments, exchange through this mechanism should be very slow, with the exception of the single experiment in which HCl had been added to the acetone.

We have confirmed this conclusion by further experiments under our conditions. In the first experiment in each of Tables 1 and 2, the solutions were kept in a 30°

TABLE 4.—TRITIUM-LABELLED ACETONE PRODUCED BY SOLUTION AT 30°C OF LiCl PELLETS IRRADIATED AT −196°C AND ALLOWED TO WARM AT ROOM TEMPERATURE

Irradiation number	Warming time	2,4-DNPH	Solution
3	30 min	60	44,000
	24 hr	15	36,000
	1 week	15	—
	1 week	12,000*	—

* Acetone containing small amount of conc. HCl.
— Not measured.

thermostat for 3 days, after which an aliquot was taken of each and the 2, 4–dinitrophenylhydrazone formed. The same solutions were continued at the same temperature for an additional 15 days, after which another aliquot was taken, and the derivative again formed. In each case, the derivatives formed after 15 additional days showed no increase in specific activity, despite the presence in each solution of approximately 200,000 d.p.m./mg of labile tritium. A separate experiment in which one of the acetone solutions was boiled overnight under reflux showed very little increase in activity in the derivative.

[2] H. C. UREY and G. K. TEAL *Rev. mod. Phys.* **7**, 34 (1935).

RESULTS

The results of the experiments involving solution of pellets in pure solvents are shown in Tables 1 and 4 for acetone and in Table 3 for ethyl alcohol and acetic acid. The experiments with pure acetone indicate that a variable amount of the tritium trapped in the LiCl crystal eventually enters chemical combination as tritium-labelled acetone. Very little activity was found in the derivatives from ethyl alcohol and acetic acid and this amount can be easily accounted for through exchange during the formation of derivatives. However, the carbon-bound activity in acetone in many experiments is much too large to be explained by exchange during derivative formation. Substantial amounts of activity do turn up in all solutions as labile hydrogen, but there is no evidence for attack of tritium upon C—H bonds except in acetone. The activity in the solutions is less than the total present in the LiCl as calculated from flux and cross-section. The remainder of the activity presumably comes off as HT gas.

Results are only approximately reproducible for pellets from the same irradiation treated in identical fashion, while the variations in activity between equivalent treatments of pellets from separate irradiations are quite marked. This lack of reproducibility occurs both in the activity as labelled acetone and in the total amount of activity in the solution. Part of the irreproducibility, especially in total solution activity, arises from the size and characteristics of the residue in each solution. However, the heterogeneous nature of the irradiated powder, the temperature inequality between pellet and solution, and the hygroscopic nature of LiCl furnished adequate opportunity for differences to arise in otherwise equivalent treatments.

The differences between separate irradiations are sizable. Irradiations number (1) and (2) were performed simultaneously after identical preparations of the samples. The irradiated pellets from number (1) uniformly gave much higher acetone activities than did the pellets from number (2). The only obvious difference between these irradiations was the elapsed time between irradiation and use—all of the pellets from number (1) were used before number (2) was opened. Elapsed time cannot be the only explanation, however, for number (3) was used sooner after irradiation than either (1) or (2).

The acetone sample from irradiation (1) with specific activity of 56,000 d.p.m./mg (over 80 per cent of the total activity in the solution) was the first acetone sample tried—solution was carried on in a 30°C thermostat with the exception of two 5 min periods during which the acetone was heated to boiling in an attempt to hasten the solution process. In subsequent experiments, the temperature was maintained constant throughout.

It is difficult to assess the effects of solvent temperature—temperatures of 0° and −78° seemed not to favour formation of tritium-labelled acetone. Results at 45–50° gave conflicting results. However, the temperature of the thermostat is only a qualitative indication of the actual temperature in the vicinity of the dissolving particles, especially in the first stages of solution before temperature equilibrium is established Comparison of the acetone activities obtained with pellets at −196°C and warmed pellets from the same irradiation (Tables 1 and 4) indicate that the reactivity of the tritium is rapidly removed by warming. Hence, the reaction leading to labelled acetone probably takes place completely during the time prior to the establishment of temperature equilibrium between the pellet and solution.

The effect of dissolved solutes upon the amount of labelled acetone formed is

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illustrated in Table 2. The formation of labile tritium through reaction with hydroxyl groups seems to compete very effectively with the reaction which forms labelled acetone.

Diphenyl ether seems to have little effect on the amount of activity showing up as acetone, while the lower activity in the presence of anethole may well be due to the double bond in the side chain of the latter. The radical scavenger, diphenyl picryl-hydrazyl, (DPPH) apparently also reduced the C—H activity from the tritium released in the solution process.

DISCUSSION

These experiments indicate that the tritium atoms in the LiCl lattice are capable of undergoing at least two reactions upon solution in acetone:

$$T + CH_3COCH_3 \rightarrow CH_2TCOCH_3 + \ldots \quad (1)$$

$$T + {=}O \rightarrow {-}O{-}T + \ldots \quad (2)$$

In addition, reaction to form HT is probable although not verified in these experiments. In solutions containing —OH groups, the reaction

$$T + {-}O \rightarrow H{-}O{-}T + \ldots \quad (3)$$

is the predominant one leading to non-gaseous products.

Reaction (1) appears to involve a reactive species of tritium. The ability of this species to undergo reaction (1) can be reduced or eliminated by altering the conditions of reaction, as by warming the lattice, varying the solvent temperature, or by adding solutes to the solvent. By inference, these alterations either reduce the concentration of this species or offer strongly competitive reaction paths which make reaction (1) negligible.

The reactivity of the tritium in reaction (1) can be explained by:

(a) Reactions of T atom trapped in the lattice.

(b) Reactions of the T^+ ion in the lattice, before solvation.

or possibly:

(c) A catalytic effect of the irradiation-damaged lattice adjacent to the trapped tritium at the time of solution.

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INFLUENCE OF FLUORINE SUBSTITUTION ON THE PROPERTIES OF METAL CHELATE COMPOUNDS—II

COPPER(II) CHELATES OF TETRADENTATE LIGANDS*

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(*Received* 28 *February* 1957)

Abstract—The ultra-violet, visible, and infra-red absorption spectra of four Schiff bases derived from β-diketones and their copper(II) chelates are described and discussed in relation to the structure of these molecules. Infra-red assignments are made where possible. The influence of fluorine substitution and ring size on the ultra-violet and visible spectra of the chelate compounds is discussed, and inter-relationships between structure, stability, and absorption spectra are suggested.

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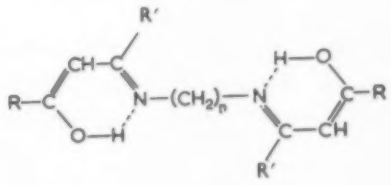
IN a previous publication,[1] the influence of fluorine substitution on the spectra of copper(II) chelates of a number of β-diketones was reported. A second class of ligands which would seem to offer structures of interest in this study are the Schiff bases derivable from diamines and β-diketones, as indicated in formula I. Thus acetylacetone or its tri-fluoromethyl derivatives, linked together by a hydrocarbon chain through Schiff-base formation, would provide a series of tetradentate chelating agents capable of conforming to the steric requirements of Cu(II) and UO_2(VI) ions The structures of the corresponding Cu(II) chelates is indicated by formula II.



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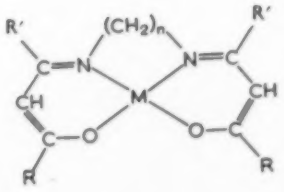

II

These compounds are analogous to those described in the first paper in this series in that they are derived from the same β-diketones.

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[1] R. LINN BELFORD, A. E. MARTELL and M. CALVIN *J. inorg. nucl. Chem.* **2**, 11 (1956).

The only ligand corresponding to formula I which has been reported prior to this investigation is bisacetylacetoneethylenediimine ($R = R' = CH_3$; $n = 2$), described by COMBES and COMBES,[2] and a number of its metal chelates studied by MORGAN and SMITH.[3] More recently a series of these substances have been prepared by MCCARTHY *et al.*[4] as model compounds for dipole moment studies. Exchange of the metal ion has been studied with bisacetylacetoneethylenediimino-Cu(II) by DUFFIELD and CALVIN[5] and with bisacetylacetoneethylenediimino-Zn(II) by LEVENTHAL and GARNER.[6]

EXPERIMENTAL

Bisacetylacetoneethylenediimine

To 20·0 g (0·2 mole) of acetylacetone dissolved in 25 ml of absolute ethanol as a moderator for the reaction, 6·0 g of anhydrous ethylenediamine diluted with an equivalent volume of absolute ethanol was added in a dropwise fashion with cooling of the reaction mixture. The resulting yellow solution was evaporated to dryness under reduced pressure with a stream of dry air at about 50°. The yellow crystalline product was recrystallized two times from toluene and two times from carbon tetrachloride. The yield was 18 g, or 80 per cent of the theoretical amount of a colourless solid which melted at 113°. It is also soluble in water, from which it crystallizes as a solvate in the form of large needles. Water is unsatisfactory for crystallization, since recovery is poor, as the result of possible partial hydrolysis of the Schiff base.

Anal. Calcd. for $C_{12}H_{20}O_2N_2$: C, 64·29; H, 8·96, N, 12·5. Found: C, 65·18; H, 8·96; N, 12·2.

Bisacetylacetoneethylenediimino-Cu(II)

To a solution of 2·0 g (0·01 mole) of copper(II) acetate monohydrate in 150 ml warm dioxane was added 3·5 g (0·015 mole) of bisacetylacetoneethylenediimine. The red solution was heated on a steam bath for 15 min, diluted with 200 ml of water, and allowed to stand overnight. The dark red needles which crystallized out were filtered off. Further dilution of the filtrate did not result in the crystallization of additional product, but a second small amount of product was recovered after evaporation of the mother liquor to a small volume. The combined relatively pure product thus obtained weighed 2·6 g, or about 90 per cent of the theoretical yield. Further purification was carried out with little loss by recrystallization from ligroin. The product was found to be very soluble in cold chloroform and carbon tetrachloride. Its melting-point was 145°C.

Anal. Calcd. for $C_{12}H_{18}O_2N_2Cu$: C, 50·4; H, 6·3; N, 9·81. Found: C, 49·2; H, 6·6; N, 9·77.

Bistrifluoroacetylacetoneethylenediimine

To 0·20 mole (30·8 g) of trifluoroacetylacetone dissolved in 200 ml of 95 per cent ethanol was added 50 ml of an ethanol solution containing 6·0 g (0·10 mole) of anhydrous ethylenediamine. The yellow solution was refluxed for 30 min, diluted with an equal volume of water, and allowed to cool. The nearly colourless crystals thus obtained were separated and a further small batch was recovered by dilution of the mother liquor with an equal volume of water and allowing it to stand for one day. The combined batches weighed 29 g, which is 87 per cent of the theoretical amount. It was further recrystallized from 50 per cent ethanol with only slight loss. It melted at 156°.

Anal. Calcd. for $C_{12}H_{14}N_2O_2F_6$: C, 43·1; H, 4·22; N, 8·44; Found: C, 42·7; H, 3·86; N, 8·28.

Bistrifluoroacetylacetoneethylenediimino-Cu(II)

A solution of 2·0 g (0·010 mole) of copper(II) acetate monohydrate in 150 ml of dioxane was treated with 4·0 g (0·012 mole) of bistrifluoroacetylacetoneethylenediimine according to the general procedure described above for the copper(II) chelate of bisacetylacetoneethylenediimine. The lavender-coloured crystalline precipitate weighed 3·8 g, or 96 per cent of the theoretical amount.

[2] A. COMBES and C. COMBES *C.R. Acad Sci., Paris* **108,** 1252 (1889).
[3] G. MORGAN and J. SMITH *J. chem. Soc.* **1925,** 2034; **1926,** 918.
[4] P. J. MCCARTHY, R. HOVEY, K. UNEO and A. E. MARTELL *J. Amer. chem. Soc.* **77,** 5820 (1955).
[5] R. B. DUFFIELD and M. CALVIN *J. Amer. chem. Soc.* **68,** 557 (1946).
[6] L. LEVENTHAL and C. S. GARNER *J. Amer. chem. Soc.* **71,** 371 (1949).

Red form. The product was dissolved in a small amount of chloroform and treated with two times its volume of warm ligroin. When the solution was slowly cooled, 1·6 g (approximately 40 per cent) of wine-red needles melting at 256° was obtained.

Anal. Calcd for $C_{12}H_{12}O_2N_2F_6Cu$: C, 36·6; H, 3·1; N, 7·12; Found: C, 36·2; H, 3·2; N, 6·95.

Blue form. An equal volume of ligroin was added to the mother liquor obtained after separation of the red product described above. After allowing the resulting solution to stand overnight, a batch of blue needles was obtained. A further small amount of the same material was recovered by evaporating the mother liquor to a small volume and adding ligroin. The combined batches of blue needles weighed 1·8 g, or about 45 per cent of the theoretical amount. Its melting point was found to be 197°, with softening beginning at 190°.

Anal. Calcd for $C_{12}H_{12}O_2N_2F_6Cu$: C, 36·6; H, 3·1; N, 7·12. Found: C, 37·0; H, 3·8; N, 7·39.

Both the red and the blue forms produced blue solutions having the same colour and shade, and showed similar solubility characteristics in polar solvents such as chloroform.

Bisacetylacetonetrimethylenediimine

To 20·0 g (0·20 mole) of acetylacetone dissolved in about 200 ml of anhydrous ethyl ether, 7·4 g (0·10 mole) of anhydrous trimethylenediamine was added dropwise with stirring and cooling. Slow addition was necessary to prevent too rapid refluxing of the ether as the result of the large heat of reaction, and a considerable proportion of the Schiff base was seen to precipitate during the addition. The reaction was completed by stirring and refluxing for 30 min and the product was isolated by cooling the mixture to 0° with a small amount of anhydrous ether. The yield of product was 18·0 g, or 80 per cent of the theoretical amount. It is very soluble in water and in most organic solvents, including toluene, carbon tetrachloride, chloroform, and the like. It is quite hygroscopic and readily absorbs sufficient moisture from the atmosphere to go into solution. It is best recrystallized from dry ether by strong cooling. The melting point was found to be 51°.

Anal. Calcd. for $C_{13}H_{22}O_2N_2$: C, 65·80; H, 9·25; N, 11·75. Found: C, 65·92; H, 9·56; N, 11·57.

Bisacetylacetonetrimethylenediimine-Cu(II)

A 2·0 g sample (0·010 mole) of copper(II) acetate was treated with 3·5 g (0·015 mole) of bisacetylacetonetrimethylenediimine according to the general procedure described above. The finely divided crystalline material obtained was dissolved in 200 ml of ligroin, evaporated to 50 ml and allowed to stand. Most of the product (1·6 g) was thus obtained as glistening greenish-black needles. Further evaporation of the mother liquor resulted in the isolation of 0·5 g more as fine dark green needles. The total yield, melting at 97°, amounted to 70 per cent of the theoretical amount.

Anal. Calcd. for $C_{13}H_{20}N_2O_2Cu$: C, 52·0; H, 6·77; N, 9·34; Found: C, 51·5; H, 6·9; N, 9·21.

Bistrifluoroacetylacetonetrimethylenediimine

A 15·4 g sample (0·010 mole) of trifluoracetylacetone was treated with 3·7 g (0·050 mole) of anhydrous trimethylenediamine according to procedure described above for the preparation of bistrifluoroacetylacetoneethylenediimine. The 13·5 g (77 per cent of the theoretical yield) of colourless crystalline product thus obtained melted at 52° and was sufficiently pure for most purposes without further purification.

Anal. Calcd. for $C_{13}H_{16}N_2O_2F_6$: C, 45·1; H, 4·63; N, 8·10. Found: C, 44·8; H, 4·87; N, 7·96.

Bistrifluoroacetylacetonetrimethylenediimino-Cu(II)

The procedure outlined for the preparation of the copper(II) chelate of bistrifluoroacetylacetoneethylenediimine was followed. The deep green dioxane reaction solution thus obtained was diluted with 1·5 times its volume of water, and 4·0 g (approximately 98 per cent of the theoretical yield) was obtained. After recrystallization from carbon tetrachloride, it was isolated in the form of dark green needles melting at 214°.

Anal. Calcd. for $C_{13}H_{14}O_2N_2F_6Cu$: C, 38·3; H, 3·4; N, 6·89. Found: C, 37·5; H, 5·8; N, 7·03.

Diethyl(ethylenebis-β-aminocrotonate)

A 26·0 g (0·2 mole) sample of ethylacetoacetate was treated with 6·0 g (0·10 mole) of ethylenediamine in the manner described above for the preparation of bistrifluoroacetylacetoneethylenediimine

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The product was obtained in the form of nearly colourless needles weighing 25·0 g, which represents 93 per cent of the theoretical yield. It was recrystallized from aqueous ethanol.

Anal. Calcd. for $C_{14}H_{24}N_2O_4$: C, 59·2; H, 8·4; N, 9·85. Found: C, 59·4; H, 8·4; N, 9·6.

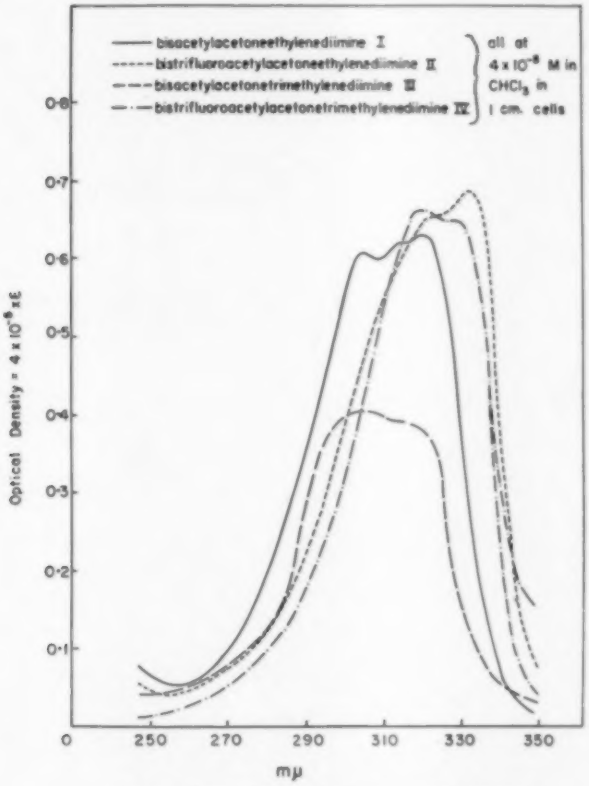


FIG. 1.—Ultra-violet absorption spectra of ligands.

Absorption spectra

Visible and ultra-violet absorption spectra were measured with a Carey Model 11 recording spectrophotometer, or with a prototype of the Beckman DK1 recording spectrophotometer, and with quartz cells of 1 cm thickness. The solutions were made up to 0·0100 M concentration by weight and progressively diluted with syringe-type pipettes until the proper concentration for absorption measurements was obtained. The spectroscopic solvent used was Eastman Kodak No. S337 Spectro-Grade chloroform.

The infra-red measurements were made with a Model 21 Perkin-Elmer recording double-beam spectrophotometer with NaCl optics. All ligands and chelate compounds were measured as Nujol mulls.

EXPERIMENTAL RESULTS

The structures of the ligands actually prepared in this investigation are indicated in Table 1. In all cases the procedures employed in their preparation were sufficiently different form those of previous investigators to warrant the brief description given in the experimental part.

The ultra-violet absorption spectra of the ligands are given in Fig. 1 and those of the corresponding Cu(II) chelates are illustrated in Fig. 2. The visible absorption

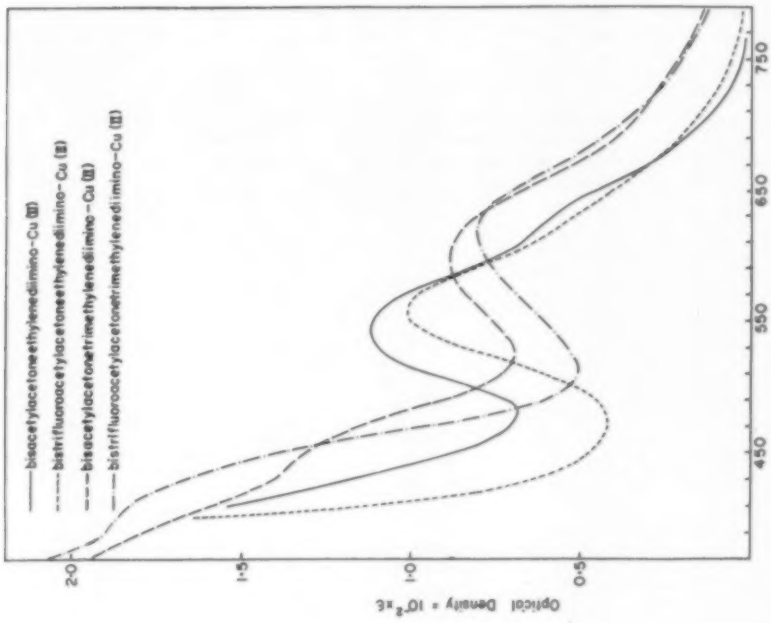


FIG. 3.—Visible absorption spectra of metal chelates.

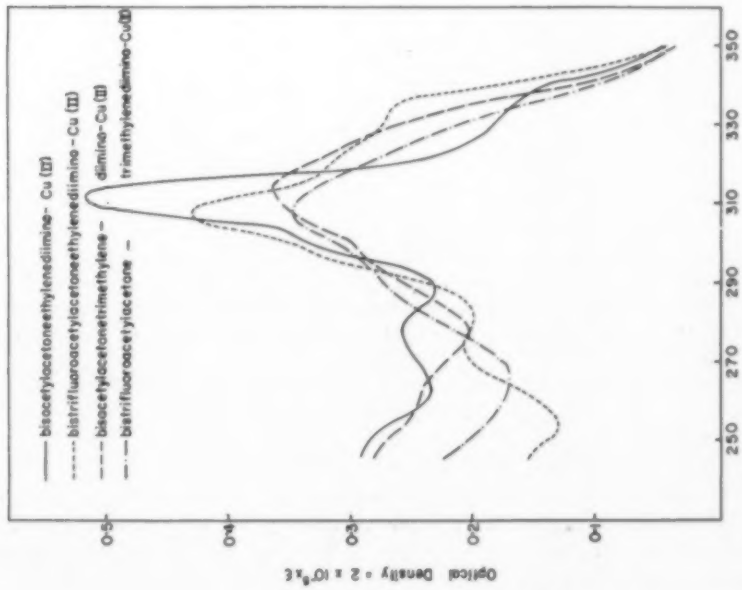


FIG. 2.—Ultra-violet absorption spectra of metal chelates.

TABLE 1.—LIGANDS AND METAL CHELATES OF THIS STUDY

Name of ligand	Formula			References	
	R	*R'*	*n*	Ligand	Cu(II) Chelate
Bisacetylacetoneethylenediimine	CH_3	CH_3	2	5, 7	6, 7
Bistrifluoroacetylacetoneethylenediimine	CH_3	CF_3	2	7	7
Bisacetylacetonetrimethylenediimine	CH_3	CH_3	3	7	7
Bistrifluoroacetylacetonetrimethylenediimine	CH_3	CF_3	3	—	—

spectra of the metal chelates are given in Fig. 3. In these diagrams, the molar extinction coefficient was determined on the basis of the assumed molecular weight of the compound, and was plotted vs. wavelength in mμ. In Table 2 are listed the wavelengths of the absorption maxima found in the visible and ultra-violet regions, and the corresponding approximate molar extinction coefficients. Frequencies are enclosed in parentheses in cases where the band is weak and occurs as a shoulder or irregularity on a much stronger band.

The infra-red absorption frequencies of both the ligands and the metal chelates are given in Table 3, with the very weak or doubtful bands indicated in parentheses. The bands have been marked arbitrarily as weak or strong on the basis of the appearance of the spectra.

DISCUSSION

Preparation of ligands and Cu(II) chelates

The methods employed in the present investigation differ from those previously reported in the use of ethanol as a moderator for the formation of the Shiff bases, and in the use of aprotic solvents for their recrystallization. For these reasons, the yields of the ligands appear to be somewhat better than those reported by MCCARTHY *et al.*[4]

All attempts to prepare Schiff bases of hexafluoroacetylacetone, ethylacetoacetate, and ethyltrifluoroacetoacetate resulted in failure. In the case of ethylacetoacetate the reaction product with ethylenediamine proved to be the diethyl ester of ethylenebis-β-aminocrotonate (III). This substance was found to produce a deep blue solution when attempts were made to convert it to the chelate by the dioxane method.

III

On dilution with water, however, cupric hydroxide precipitated. Apparently the metal chelate formed in the organic phase is relatively unstable, and breaks up in water solution.

Since no condensation was obtained between hexafluoroacetylacetone and ethylenediimine, an attempt was made to prepare the desired chelate compound

TABLE 2.—ABSORPTION BANDS OF $CHCl_3$ SOLUTIONS IN THE VISIBLE AND ULTRA-VIOLET REGIONS

Compound	Molarity	λ_{max}	ε_{max}
I Bisacetylacetoneethylenediimine	4×10^{-5}	305	15,000
	4×10^{-5}	321	15,800
II Bistrifluoroacetylacetoneethylenediimine	4×10^{-5}	322	16,200
	4×10^{-5}	337	17,000
III Bisacetylacetonetrimethylenediimine	4×10^{-5}	305	10,000
		320	9,500
IV Bistrifluoroacetylacetonetrimethylenediimine	4×10^{-5}	321	16,500
	4×10^{-5}	331	16,100
V Bisacetylacetoneethylenediimino-Cu(II)	2×10^{-5}	(~246)	—
		276	13,000
		(299)	—
		312	26,000
		(336)	—
	10^{-2}	543	112
		(635)	—
VI Bistrifluoroacetylacetoneethylenediimino-Cu(II)	2×10^{-5}	274	10,600
		(295)	—
		308	21,600
		(326)	—
		(334)	—
	10^{-2}	555	101
VII Bisacetylacetonetrimethylenediimino-Cu(II)	2×10^{-5}	(258)	—
		(298)	—
		314	18,500
	10^{-2}	376	950
	10^{-2}	(460)	—
		600	89
VIII Bistrifluoroacetylacetonetrimethylenediimino-Cu(II)	2×10^{-5}	(290)	—
		308	17,500
	10^{-2}	(450)	—
		618	81

directly by combining cupric acetate with ethylenediamine and hexafluoroacetylacetone under varying conditions of solvent and temperature. In all cases the only reactions which were detectable corresponded to separate reactions of the metal ion with ethylenediamine and with the β-diketone.

The general procedure employed for the preparation of the metal chelates, involving formation of the compound in dioxane and precipitation by the addition of water, differs considerably from the methods previously employed,[4] which usually

TABLE 3.—INFRA-RED ABSORPTION BANDS OF NUJOL MULLS*

Region	I eA	II eT	III tA	IV tT	V Cu-eA	VI Cu-eA	VII Cu-tA	VIII Cu-tT	IX
O—H, N—H	3120 *b*	3140 *s*	(3220)	3160 *s*		(3400)	3500 *s*	(3360)	
	(2700) *b*	(3060)				(3140)			3260 *s*
	(2320)	(2340)	(2350)	(2320)	(2320)	(2350)	(2340)	(2340)	
		(1710)	(1665)						1730 *w*
C···O,	1615 *s*	1612 *a*	1610 *s*	1615 *s*			1673 *s*		1645 *s*
C···C,	1585 *s*	1585 *s*	1570 *s*	1590 *s*	1592 *s*	1627 *s*	1645 *w*	1631 *s*	1607 *s*
						1573 *s*	1588 *s*		1565 *w*
C···N	(1550)	1533 *s*	(1550)	(1550)				1552 *s*	1545 *w*
	1525 *s*	(1510)	1516 *s*	1525 *w*	1515 *s*	1545 *s*	(1535)	(1515)	1510 *s*
			1448 *s*	1450 *s*	1440 *w*	(1510)	1512 *s*	(1490)	
		1395 *w*	1357 *s*	1395 *w*	1422 *s*	(1443)	1415 *s*	(1452)	1445 *s*
C—N	1360 *w*	1345 *w*	(1300)	1365 *w*	1356 *s*		1360 *s*		1368 *w*
			1320 *w*	1317 *w*					1338 *s*
	1295 *s*	1287 *s*	1285 *s*	1292 *s*	1285 *s*	1300 *s*	1325 *w*	1305 *s*	1305 *s*
	1258 *w*	1267 *w*	1247 *s*	1250 *a*	(1255)	1256 *s*	1288 *s*	1273 *w*	1290 *s*
	1227 *w*	1248 *s*	1215 *s*		1229 *s*	1228 *s*	1253 *s*	1255 *w*	1270 *s*
							1235 *s*		
C—C	1208 *w*	1208 *s*	1200 *w*		(1215)		1217 *s*	1218 *s*	1225 *s*
		1190 *s*		1195 *s*			1200 *s*		
						1183 *s*		1192 *s*	1183 *w*
		1135 *s*	1140 *s*	1137 *s*		1150 *s*	1145 *s*	1178 *s*	1168 *s*
	1145 *w*					1130 *s*	(1130)	1151 *s*	1150 *s*
		1120 *s*		1115 *s*	1117 *s*			1128 *s*	
	1087 *s*	1080 *s*	1092 *s*	1085 *w*	1073 *s*	1105 *w*		1100 *s*	1115 *s*
	1020 *s*	(1055)		1070 *w*	1043 *s*	1093 *s*	1090 *w*	1087 *w*	1092 *s*
			1028 *s*	1025 *w*	1028 *w*	1073 *w*	1043 *s*		1067 *s*
		1007 *w*	1000 *s*		1018 *s*	(1035)	1020 *s*	1023 *w*	(1037)
	975 *s*		975 *w*	990 *w*	988 *s*	1020 *w*	1000 *w*		1020 *s*
			956 *s*		948 *s*		(970)	(970)	978 *s*
	940 *w*	943 *s*	933 *s*	903 *s*		(950)	955 *w*		
							945 *s*		
		880 *s*	887 *w*	888 *s*	(880)	897 *s*	(932)		935 *w*
	850 *s*	(870)	865 *w*	875 *w*				895 *s*	
				848 *s*		865 *s*	872 *s*	865 *w*	
	835 *w*	832	(830)	830 *w*					830 *w*
				803 *w*	805 *w*				
		780 *w*	780 *s*	785 *s*		792 *s*	(792)	783 *w*	777 *s*
		775 *s*		767 *s*		787 *s*	785 *s*	773 *s*	
	740 *s*		750 *s*		753 *s*	742 *w*			757 *w*
		755 *s*		747 *s*			760 *s*	733 *s*	
	720 *w*								
		723 *s*	725 *s*	725 *s*	738 *s*	732 *s*	(740)	720 *w*	720 *s*
			645 *w*		670 *w*		670 *w*	(660)	
					645 *w*				

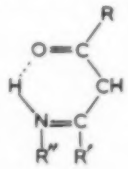
* eA = *e*thylene diimine-bis-*A*cetylacetone
eT = *e*thylene diimine-bis-*T*rifluoroacetylacetone
tA = *t*rimethylene diimine-bis-*A*cetylacetone
tT = *t*rimethylene diimine-bis-*T*rifluoroacetylacetone
Bands are classed arbitrarily as *s*-strong; *w*-weak; or *b*-broad.

involved combination of the ligand with the freshly precipitated metal hydroxide or hydrous oxide. The method used in this investigation gives yields which are at least as good as those previously described.

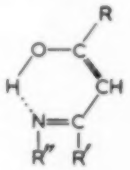
It is interesting to note that the Cu(II) chelate of bistrifluoroacetylacetone-ethylenediimine was obtained in two forms by fractional crystallization from chloroform and ligroin. The less-soluble, red form, had a melting point 66° higher than the more-soluble, blue compound. The infra-red, ultra-violet, and visible spectra (in chloroform) were found to be identical, and analytical results were also the same within experimental error. These substances are, therefore, probably crystal modifications of the same compound. In accordance with its lower solubility and higher melting point, it is possible that the red modification involves intermolecular interactions which are absent in the blue one, and that these interactions probably involve metal metal forces. The fact that the red colour is lost in such polar solvents as chloroform and acetone, seems to support this point of view, particularly since both substances give identical blue solutions.

Ultra-violet absorption spectra

All of the ultra-violet absorption spectra in Figs. 1 and 2 are high-intensity *K*-type bands arising from electronic transitions in conjugated systems of the type shown in formulas I and II. The characteristic double bands of the ligands would at first seem to arise naturally enough from the two tautomeric forms possible for each H-bonded ring of the ligand, indicated by formulas IV and V.



IV



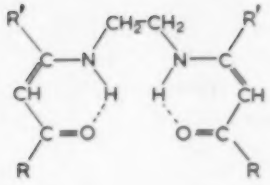
V

However, independent measurements by UENO and MARTELL[7] have shown that the relative intensities of the two bands are only slightly altered in 0·1 M NaOH solution. It seems probable, therefore, that each band is due to electronic transitions in the single conjugated system:

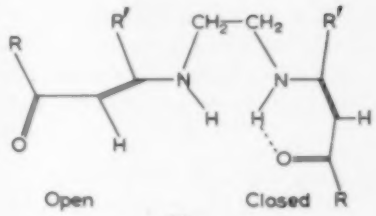
and that this is perhaps not very much affected by H-bonding to the oxygen or nitrogen.

The presence of two or three bands may possibly arise from different relative arrangements of the two conjugated systems arising from rotation through the ethylene or trimethylene bridge. Thus, the H-bonded rings may be relatively far apart as in formula I, or close together as in formula VI. This may be coupled with differing interactions arising from the isomeric "closed" or "open" forms as in formula VIa.

[7] K. UENO and A. E. MARTELL *J. phys. Chem.* **61**, 257 (1957).



VI



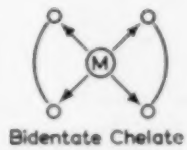
VIa

As in the case of the bidentate ligands discussed previously,[1] the effect of introducing one trifluoromethyl group is to increase the wave lengths of the absorption maxima, and to increase somewhat the tendency to enolize. Because of the lack of a considerable increase in intensity on the addition of alkali, noted above, it seems that all of the ligands are nearly completely enolized. As a first approximation, it seems that bisacetylacetoneethylenediimine must be at least 90 per cent enolized. If one then assumes that the corresponding trifluoro compound is 100 per cent enolized, it is apparent from the relative absorption coefficients listed in Table 2 that substitution of the trifluoromethyl group results in little or no increase in the absorption intensity. It seems more logical, therefore, to assume complete enolization of both ligands derived from ethylenediamine, and an increase of 10 per cent in the intensity of the absorption resulting from the introduction of a trifluoromethyl group at one end of the conjugated system.

The large increase of intensity observed as the result of introduction of a trifluoromethyl group into the Schiff base derived from trimethylenediamine could be due to relatively incomplete enolization of the parent compound, and to what appears to be complete enolization of the trifluoromethyl derivative.

Unlike the bidentate ligands described previously, the ultra-violet spectra of the metal chelates of the Schiff bases bear little resemblance to those of the ligands. Instead of the simple double or triple bands present in the ligand, the metal chelates have complicated systems of at least five bands in each case, with one of much higher intensity than the others. The absorption curves shown in Fig. 2 indicate that the spectra can be divided into two similar pairs: 1, those involving the Schiff bases derived from ethylenediamine; and, 2, the chelates derived from trimethylenediamine. It is apparent that changing the number of carbons in the hydrocarbon bridge from 2 to 3 has a greater influence on the spectra than substituting a trifluoromethyl group in each six-membered metal chelate ring.

It is perhaps not unreasonable that the spectra of the tetradentate chelates should differ so greatly from those of the β-diketones, when one considers the differences in the arrangement of the dipoles and charges in these two classes of compounds. If one makes the reasonable assumption that both classes of chelate compounds are square planar, one has the following arrangements of dipoles and charges about the metal ion:



Bidentate Chelate

Tetradentate Chelate

Thus, it is seen that the influence of the metal on the bidentate β-diketones is more symmetric than the effect on the ends of the conjugates systems in the Schiff bases. The greater number of distinct π-system energy levels in these compounds, indicated in Fig. 2, is probably related to that decreased symmetry.

Visible spectra

The absorption spectra of the copper(II) chelates in the visible region, shown in Fig. 3, are similar to those of the copper(II) chelates of the bidentate ligands, and presumedly arise from the same type of 3*d*-orbital transitions. One would expect that the polar fields of the donor atoms of the Schiff bases would be more effective than the simple β-diketones in removing the *d*-orbital degeneracy of Cu(II) because of the greater interaction of the former with the metal ion. That this is actually the case may be seen qualitatively in the fact that the frequencies of the principal absorption bands in the visible region occur at much shorter wavelength and are much more intense for the Schiff bases. In some cases the absorption maxima of the β-diketone is found displaced 100 mμ or more toward longer wavelength than that of the Schiff base derived from the same β-diketone.

The absorption spectra in Fig. 3 indicate that the influence of trifluoromethyl groups is to shift the absorption bands of the metal chelates to longer wavelengths. This is the same direction as the shifts observed in the Cu(II) chelates derived from the bidentate ligands. As indicated previously, this shift to the red correlates with a decrease in stability of the metal chelate and decreased interaction of the charges of the ligand with the electrical field of the metal ion.

Perhaps even more interesting is the greater increase in wavelength of the visible copper(II) band when the ethylene bridge is replaced by a three-carbon chain. It is well known that increasing the size of the metal chelate ring formed between the two basic nitrogen atoms decreases the stability of the chelate compound. The common explanation of this correlation between stability and ring size, involving an entropy effect, does not seem to offer an explanation of the shift in the spectra. Unlike the trifluoromethyl groups, which obviously influence the donor-metal interaction by an inductive removal of electrons, it is difficult to see how the size of the aliphatic chelate ring, *per se*, could affect so greatly the metal ion transitions. However, it is obvious from the shifts in Fig. 3 that the influence of increasing ring-size is greater than that resulting from the substitution of trifluoromethyl groups on the ligand, in agreement with the conclusions drawn above from the ultra-violet spectra. A possible explanation would be that steric considerations involving the three metal chelate rings as a whole might actually force the nitrogens closer to the Cu(II) ion when the central (diamine) ring contains five members than when the ring contains six atoms. Greater proximity between the nitrogens and the Cu(II) ion in the ethylene diamine derivatives would result in more spreading of the *d*-orbital energy levels of the Cu(II) by the amino-group charges and dipoles. It is quite likely that insertion of an extra methylene into the ethylenediamine bridge produces some more profound change in the chelate bi-ring structure.

Infra-red spectra

All of the free ligands have a broad absorption band near 3150 cm^{-1} which is assigned to the NH or OH stretching frequency. The broadness of these bands is a good indication that the group is involved in hydrogen-bond formation.

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The effect of introducing CF_3 groups in the ligands results in a higher NH or OH stretching frequency, possibly indicating weaker hydrogen bonds. This effect may be due to the interference of the electron-attracting trifluoromethyl group with the resonance of the conjugated system to which it is attached. It is also possible that the basicity of the donor atoms is also decreased sufficiently by fluorine substitution to affect hydrogen bonding or that the frequency shift is primarily the result of direct influence through the hydroxyl oxygen or amino nitrogen.

The foregoing assignment of the broad bands in the 3200–3100 cm^{-1} region is further strengthened by the disappearance of these bands in the metal chelates, in which the enolic or amino hydrogens are completely displaced by the copper(II) ion.

It is interesting that, unlike the β-diketones discussed previously, the Schiff-base ligands in the present investigation do not show free carbonyl bands. All of the Schiff bases have strong bands in the frequency range 1610–1615 cm^{-1}, which can only be due to H-bonded carbonyl stretching vibrations. These appear at lower frequencies than do the corresponding bands of the β-diketones, indicating stronger hydrogen-bonding in the former compounds.

Another band, in the 1570–1585 cm^{-1} region, sometimes occurring with a subsidiary band, may be assigned to C=C stretch in the H-bonded rings. It is to be noted that these frequencies are considerably lower than the corresponding bands of acetylacetone and other β-diketones, possibly as a result of stronger resonance of the conjugated rings in the Schiff bases.

The bands appearing at 1525 ± 10 cm^{-1} are assigned to C=N stretching vibrations displaced from their usual positions at 1690–1640 cm^{-1} as the result of strong hydrogen-bonding. These absorptions are, of course, absent in the spectra of the β-diketones discussed in the first paper of this series. The band appearing at 1510 cm^{-1} in the spectrum of the crotonic acid derivative, V, is probably not due to $\diagdown$C=N$\diagup$ stretch, since this group must be absent, but may be due to an N—H deformation vibration which usually appears in this region. Although these assignments correspond to those of UENO and MARTELL[8] for a somewhat different series of compounds, it is quite possible that the true C=C and C=N assignments have been inverted in all the Schiff bases.

The bands observed in the 1300–1500 cm^{-1} region are likely CH_3 and CH_2 deformation vibrations. A number of bands in the 1120–1282 cm^{-1} region, which appear only in the spectra of the trifluoro derivatives, may be assigned to C—F stretching vibrations.

The structure assigned to the crotonic acid derivative, formula III, is in conformity with the presence of the ester carbonyl band at 1730 cm^{-1}, as well as a band at 1645 cm^{-1} which may be due to the H-bonded carbonyl group. The lower-frequency bands may be due to C=C stretching vibrations of the various modifications (H-bonded, etc.) which are present. There may even be weak contributions from small amounts of the imino tautomer.

[8] K. UENO and A. E. MARTELL *J. phys. Chem.* **59**, 998 (1955).

J. Inorg. Nucl. Chem., 1958. Vol. 5, pp. 182 to 189. Pergamon Press Ltd., London

THE MICROSCALE PREPARATION AND MICROMETALLURGY OF PLUTONIUM METAL*

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Abstract—An historical survey of the methods used at the Metallurgical Laboratory in the first preparations of plutonium metal are given. The techniques and conditions necessary for the preparation of the metal are described in detail, and the effects of the several variables temperature, reductant, crucible material, etc. are discussed. These methods are capable of and have been extended to the preparation of small amounts of the highly radioactive heavy elements. The method of determining the density of microgram amounts of plutonium metal is described and the experimentally determined densities of plutonium metal are given.

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THIS presentation of the techniques which led to the first successful preparation of plutonium metal is made not only for its historical interest, but also to exhibit the utility and advantages of these methods for their possible applications to other problems. These studies did indeed provide data essential to the macroscale technology of plutonium metal production which followed very soon thereafter at Los Alamos.[1] However, microscale metallurgical methods are of continuing applicability in the isolation and investigation of synthetic and other rare elements; especially so with intensely radioactive materials in that adequate protection for personnel may be more readily achieved.

A major chemical problem in the development of the release of nuclear energy was the preparation on the microgram scale of globules of plutonium metal suitable for the investigation of its physical and chemical properties. Micrometallurgy on this scale was unprecedented; an entirely original approach was necessary. The uncertainty inherent in the prediction of the physical and chemical properties of a new element (in a series the very nature of which was still under speculation), the exceedingly small amounts of plutonium available, the doubt as to the identity and composition of compounds to be reduced, and the extreme health hazard of traces of the finely divided solids aggravated the problem. The complex allotropy of plutonium,[1,2] which was not then suspected, also contributed to the difficulty of these investigations.

Preliminary experiments were made on "stand-in" compounds which it was hoped would stimulate the behaviour of plutonium compounds in reduction to the element.

The objective was reduction on the μg scale with high yields of metal in a single globule. A variety of methods was tested, including reduction with atomic hydrogen,

* The investigations summarized in this paper comprise microchemical and micrometallurgical studies on plutonium completed in 1943–44 under pressure of wartime conditions at the Manhattan Project "Metallurgical Laboratory" operated by the University of Chicago for the U.S. War Department. This work has only recently been declassified by the U.S. Atomic Energy Commission.

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[1] C. S. SMITH *Metal Prog.* **65**, 81 (1954).
[2] C. S. SMITH *Phys. Rev.* **94**, 1068 (1954).

electrolytic reduction in aqueous and fused-salt systems, and thermal reduction of halides with alkali and alkaline earth metals; only the last mentioned proved successful and is described here. On the basis of the limited data available, uranium compounds were selected as probably representative of the chemical reactivity and physical properties of the analogous plutonium compounds. UF_4 was chosen because of its stability, non-hygroscopicity, and comparative non-volatility. It was anticipated that PuF_4 would have a similar set of desirable properties.

The first attempted reductions[3] were performed by distilling alkali metals onto uranium compounds placed in the tip of glass micro-cones *in vacuo* and removing excess alkali metal by heating the mixture gently with a flame. Further inconclusive attempts to reduce a few μg of UF_4 and PuF_4 to metal by treating it with sodium in evacuated glass capillaries[4] emphasized the need for practical criteria for identification of metal on the micro scale. Methods involving the metallic characteristics of malleability, high density, lustre, and especially the formation of a hydride were adapted to microscale work.

The first unequivocal production of plutonium metal was made in November 1943.[5] About 35 μg of PuF_4 were transferred to a small thoria crucible on the tip of a sharp needle. About ten times the stoichiometric amount of barium metal freshly cut under xylene was placed in a larger crucible, the small crucible was inserted on top of the reductant, the outer crucible cap inserted, and the entire crucible assembly placed in a microfurnace and fired to 1400°C in a high vacuum. A number of 3 μg plutonium-metal globules were formed. The metal had a silvery lustre, a density of about 16 g/cm^3, and rapidly absorbed hydrogen at about 210°C to form a black powder subsequently identified as PuH_3.[6]

EXPERIMENTAL

The ceramic double crucible system. The reaction between condensed phases of reactants was generally violent and tended to yield dispersions of metal and slag. Techniques were therefore developed whereby only the reductant vapour came in contact with the halide to be reduced.[5,7,8]

Although originally the small crucible with its charge of plutonium halide was placed on top of the reductant metal, after subsequent experimentation, the arrangement of the double crucible system was modified to that shown in Fig. 1.[9] This reduced the tendency of the volatilizing reductant to agitate the inner crucible and disturb its contents. To this end the top of the inner crucible was slightly castellated, the inner crucible was placed on the bottom of the outer crucible, and was covered with a thin plate of ceramic to separate its contents from the solid reducing agent above it. A conical cap partially sealed the system and permitted the reductant to develop pressure and subsequently to escape gradually.

The most generally satisfactory crucibles were made of beryllia (BeO). These were fabricated by making a paste of finely ground fused beryllia with 6 M nitric acid. The stiff paste was formed into crucibles with the aid of stainless steel mandrels.

[3] P. L. Kirk and R. S. Rosenfels *Met. Lab. Report* CK–514 (March 1943).
[4] P. L. Kirk and R. S. Rosenfels *Met. Lab. Report* CK–591 (April 1943).
[5] H. L. Baumbach, S. Fried, P. L. Kirk and R. S. Rosenfels *Met. Lab. Report* CK–1145 (Dec. 1943).
[6] S. Fried and A. Dirksen *Met. Lab. Report* CK–1372 (March 1944).
[7] H. L. Baumbach, R. S. Rosenfels and P. L. Kirk *Met. Lab. Report* CK–736 (June 1943).
[8] H. L. Baumbach, R. S. Rosenfels and P. L. Kirk *Met. Lab. Report* CK–987 (October 1943).
[9] S. Fried and E. F. Westrum, Jr. *Met. Lab. Report* CK–1512 (April 1944).

After gradual air drying, they were slowly fired to 1000° in a muffle furnace. They were then shaped and bored to exact size and then fired and outgassed in high vacuum. Beryllium oxide is extremely toxic and care should be taken in handling this material. The outer crucibles and caps were fired to 1800°C for greater hardness and strength;

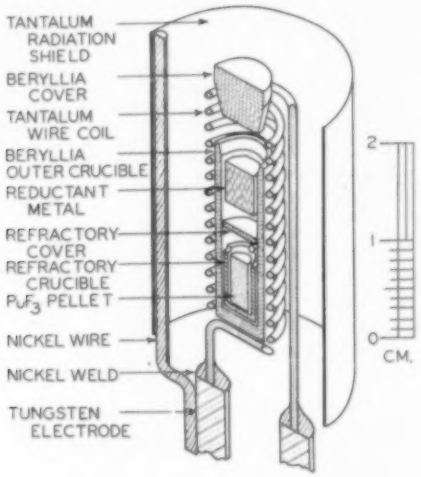

FIG. 1.

the inner crucibles were partially vitrified by heating to 1600°C for an hour in order to minimize penetration by the plutonium metal and yet preserve the degree of porosity useful in absorbing the slag. Thoria crucibles were similarly fabricated, except that the paste was made with ground fused thoria and 50 per cent thorium nitrate solution.

The high vacuum furnace. The original furnaces[5] consisted of a helix of tungsten wire imbedded in beryllia. The shielded tantalum furnace[9–11] (Fig. 1) had several advantages in that it was more efficient, more readily outgassed, and the tantalum coil was not subject to embrittlement from repeated heating cycles. The furnace was controlled with an autotransformer in series with a step-down transformer. Crucible temperatures of about 1600°C were obtained using 14 A at 12 V. These furnaces were operated *in vacuo* of 10^{-6} mm Hg in air-cooled 500 cm^3 bulbs with water-cooled, standard taper joints to permit removal of the furnace assembly. The bulbs were attached to a vacuum system using Apiezon-W wax on large standard-taper joints permitting pumping speeds of the order of 20 l./sec at the furnace position. Because water and oxygen react with plutonium halides to produce compounds difficult to reduce, it was found necessary to outgas the furnace and crucible system for about an hour at 1600°C at 10^{-5} to 10^{-6} mm Hg prior to loading and to break the vacuum with argon purified by passage over uranium turnings at 800°C.

Reactants. Plutonium tetrafluoride was prepared by the hydrofluorination of PuO_2 (prepared from air dried plutonium hydroxide[12]) with hydrogen free anhydrous

[10] E. F. WESTRUM, JR. *Met. Lab. Report* CK–1586 (May 1944).
[11] E. F. WESTRUM, JR. *Met. Lab. Report* CK–2495 (Jan. 1945).
[12] E. F. WESTRUM, JR. *The Transuranium Elements, National Nuclear Energy Series* Vol. 14B, Paper 6.57. p. 936. McGraw-Hill, New York (1949).

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HF at 600°C. Plutonium trifluoride was prepared by techniques similar to those previously described for americium trifluoride.[13]

Experimental reduction technique.[14] To prevent oxidation of the surface of the reductant metal and adsorption of water on the outgassed crucibles, the handling of crucibles and the entire loading procedure was performed in a dry box with an anhydrous nitrogen atmosphere provided with an evacuable air lock and a horizontal plate glass top to facilitate operation under a stereoscopic dissecting microscope. Small amounts of anhydrous plutonium compounds (5–200 μg) were loaded into the inner crucible on the tip of a tungsten needle. In the larger scale reductions (e.g. 1–50 mg), it was found effective to compress (to about 10^4 kg cm^{-2}) the plutonium halide into small cylindrical pellets 0·5–1·5 mm in diam. with hardened steel dies in a hand press. This procedure resulted in better agglomeration and higher useful yield of the product metal. Intermediate amounts were handled with a small spatula. The loaded inner crucible was dropped inside the larger one and the small refractory disc or cover dropped in on top. A freshly cut piece of pure barium (in large stoichiometric excess) was dropped in and then the previously fitted refractory cap plugged tightly in place. The entire crucible assembly was rapidly transferred to the furnace which was evacuated on the high vacuum line until the pressure was 10^{-5} mm Hg or better. This evacuation required 15–20 min.

Firing of the furnace system was achieved by applying the full voltage to the coil. In about 10 sec the coil reached its maximum temperature; the crucible system required much longer. Very soon after the crucible reached red heat, the barium vaporized, gradually escaped from the crucible, and condensed as a mirror on the bulb walls. Under certain conditions a luminous green discharge existed as long as there was an appreciable vapour pressure of barium. After approximately 1 min, or longer if the continuing escape of barium was indicated by the discharge, the current was cut off, and the system was allowed to cool under vacuum. The last stages of the cooling process were aided with admission of highly purified argon. After removal from the furnace, the crucibles were opened and the metallic globule(s) of metal removed. The slag was generally absorbed within the pores of the inner crucible. Occasionally, the metal would partially wet the crucible and was removed only with difficulty. Fragments of refractory adhering to the metal could be removed under xylene with a sharp tungsten needle.

Results of reductions. A series of studies on the reduction of PuF_4 with Ba[9] in BeO crucibles indicated that at least partial reduction took place at furnace temperatures in excess of 900°C. Optimum results were obtained at about 1150°C. Although a single globule was desired, the results were considered acceptable if the over-all yield of compact globules was high and each globule represented at least 20 per cent yield. Reduction of $PuCl_3$ to metallic plutonium was achieved[10,15] in fair yield by the action of Li, Na, K, Ba, and Ca. However, the reductions of the chloride with reductant vapour on the 5–8 mg scale did not produce large particles (i.e. larger than 0·5–1·0 mg) of metal, even with pelleted chloride. This is attributed to the higher volatility of the $PuCl_3$ as compared to PuF_4. An attempt was made to increase the

[13] E. F. Westrum, Jr. and L. Eyring *J. Amer. chem. Soc.* **73**, 3396 (1951).
[14] A series of photographs of microscale plutonium metal production techniques appears in *Life* **21**, No. 2, 68 (8 July 1946) and in *Life International* **1**, No. 1, 30 (22 July 1946).
[15] E. F. Westrum, Jr. *Met. Lab. Report* CK-1701 (June 1944).

yield by bringing the halide into direct contact with the molten reductant in the outer crucible at lower temperature. This resulted in less sublimation of $PuCl_3$ formation of larger particles, and increased yield. $PuBr_3$ also has been reduced to Pu metal with calcium.[9] Two attempted reductions of PuOCl with potassium yielded only the phase identified both by its characteristic semi-metallic appearance and by X-ray diffraction analysis as PuO.[9] Attempted reductions of PuO_2 with Na and Mg vapour at about 1200°C did not show evidence of reduction; Ca and Li vapour at

TABLE 1.—REDUCTION OF PLUTONIUM TRIFLUORIDE

Reductant	Inner crucible	Furnace temperature	Results
Ba	BeO	1250°C	Single piece of metal, good yield.
Ba	La_2O_3	1250°C	Single piece of metal, fair yield.
Ba	CaO	1250°C	Poor results, metal surface pitted.
Li	BeO	1350°C	Good results, metal in one piece.
Ca	BeO	1250°C	Obtained 60·4 mg metal from 85·3 mg PuF_3; 88 per cent yield.
Ca	BeO	1450°C	One piece of metal, 33·2 mg 92 per cent yield, density: 18·7.
Li	Graphite	1000°C	Formation of PuC (and possibly Pu_2C_3) only.

1200°C yielded only partial reduction to a phase tentatively indentified as Pu_2O_3.[16] Plutonium fluorides were reduced with Ba in La_2O_3, tantalum, and tantalum nitride.[10,15] However, the product metal wetted both Ta and TaN and could not be separated from either.

Plutonium trifluoride is easily prepared, has desirable physical characteristics, and has been more thoroughly investigated from the standpoint of metal production of the mg scale in this laboratory than have the other halides. Table 1 summarizes the results of the influence of various conditions on the reduction of PuF_3. Yields were excellent and the few failures could generally be traced to faulty technique or secondary reactions with crucible material. Almost 200 microscale reductions of PuF_3 were made in beryllia.

Metal produced in thoria crucibles regularly revealed appreciable contamination by thorium. Beryllium oxide, however, yielded very pure plutonium metal. Spectrographic analyses of plutonium made in beryllia crucibles by barium reduction on the 1 mg scale indicated (in p.p.m.) from 1–4 of Be, 1000 of Ca, 250 of Mg, and less than 250 of Ba, with no other metals detectable.[10] Atmospheric contamination from building construction materials is believed to be in part responsible for the high calcium content. Other crucible materials (cf. Table 1) were also studied with respect to their practicability for metal production. Crucibles prepared from vacuum-fired moist La_2O_3 showed considerable promise, but the hydroscopicity complicates the handling in air. Crucibles of CaO prepared both of reagent oxide and of dense St. Genevieve limestone (some silica present) were less satisfactory.

Tests of sulphide refractories for metal production. Sulphide refractories suitable

[16] E. F. WESTRUM, JR. *Met. Lab. Report* CN-2159 (October 1944); W. H. ZACHARIASEN Private communication.

for the fabrication of crucibles tend to be resistant to reduction, have high melting points and relatively low volatilities. Tests were, therefore, made on the practicability of utilization of a series of sulphide crucibles prepared by a group of scientists at the University of California at Berkeley under the direction of EASTMAN *et al.*[17] The tests were made on the mg scale using high purity calcium metal as reductant. Barium was also tried on barium sulphide refractories. A tantalum liner of 2 mil thickness was interposed between the sulphide inner crucible and the beryllia outer crucible to avert the possible formation of low melting eutectics. Without the use of such a liner a CeS crucible completely fused into the beryllia during out-gassing below 1700°C.

The crucible systems, furnace, and bulb were degassed for approximately 1 hr at crucible temperatures of 1600–1700°C at 2×10^{-6} mm of Hg. After out-gassing, the crucibles were cooled to room temperature and argon was admitted to break the vacuum. The crucible system was then rapidly transferred to a nitrogen-filled dry box, loaded with pelleted PuF_3 and calcium, and replaced in the furnace. After evacuating to about 2×10^{-6} mm of Hg the actual firing was done by raising the temperature of the crucible to 1250–1350°C within 30 sec. It was noted that reduction occurred within an additional 15 sec, and the excess calcium distilled from the crucible forming a sharply defined mirror on the top and bottom of the glass bulb. The crucible system was maintained at this temperature for a total time of 4·5 min and was then allowed to cool to room temperature before breaking the vacuum.

Upon completion of the reduction the products of the reaction were examined microscopically *in situ* to note any evidence of reaction, wetting, pitting, etc. Specimens of the plutonium metal were also examined metallographically and their hardness determined with an Eberbach micro hardness tester. Other samples were submitted to the analytical section for spectrographic and chemical analyses. The overall judgment on the relative suitability of these refractories is as follows: $BaS_{0\cdot98}$—unsatisfactory; $ThS_{1\cdot77}$ and $ThS_{0\cdot97}$ (5 per cent ThO_2, 0·3 per cent MoO_2)—poor; $ThS_{1\cdot50}$, $ThS_{1\cdot00}$, and $ThUS_2$—satisfactory; $Th_{0\cdot32}Ce_{0\cdot65}S$, $ThCeS_2$—excellent.

Spectrochemical analyses on the metal produced in any of the cerium and/or thorium refractories revealed that the plutonium contained $0\cdot0 \pm 0\cdot2$ per cent of cerium and $0\cdot0 \pm 0\cdot04$ per cent of thorium. A few of the metal samples showed traces (less than 0·01 per cent) of beryllium and calcium. In the reductions in $BaS_{0\cdot98}$ crucibles, barium was present to more than 5 per cent in some samples of the calcium-reduced material. Less than 0·1 per cent of barium was present in the product obtained by barium reductions in $BaS_{0\cdot98}$ crucibles. No other elements were found to be present in concentrations greater than in the blank determinations on the reagents and electrodes.

Colorimetric analysis for sulphur showed less than 200 p.p.m. of sulphur (the practical limit of sensitivity of the method) for all metal produced in the various sulphides with the exception of the two reductions in barium sulphide crucibles. Analysis[15] by chemical and X-ray diffraction methods indicated that the product from calcium reduction of plutonium in a BaS crucible was an impure and inhomogeneous PuS. The plutonium reduced with barium in the other barium sulphide crucible showed $0\cdot0 \pm 0\cdot08$ per cent sulphur.

[17] E. D. EASTMAN, L. BREWER, L. A. BROMLEY, P. W. GILLES and N. L. LOFGREN *J. Amer. chem. Soc.* **72**, 4019 (1950).

The density of plutonium metal. The density of plutonium metal was determined when only mg globules of metal were available using the micro-pycnometric method developed by KIRK and his associates.[5]

A series of uniform cylindrical capillaries having internal diameters of 100–200 μ were drawn. These were sealed shut at intervals of about 5 cm and cut within 5 mm of the seal, forming a short cup with a long stem The diameter of each cup was accurately calibrated with an ocular micrometer with about 100 $\times$ magnification.

A capillary was selected with an internal diameter slightly larger than the metal globule. The metal was weighed on a quartz fibre torsion microbalance[18] to an accuracy of about 0·01 μg. The capillary was loaded with a small droplet of dibutyl phthalate (chosen for its low volatility) which was centrifuged to the bottom of the cup. The position of the meniscus was determined relative to a reference mark to an accuracy of about 0·001 mm. The metal particle was then inserted with a micro-manipulator and centrifuged to the bottom of the cup. The new meniscus position was determined with respect to the reference mark and the movement used in conjunction with the capillary calibration to determine the volume displaced by the metal. This volume and the weight were then used to calculate the density. The method was tested by determining the specific gravity of Pt spheres (21·5 $\pm$ 0·3) and of mg quantities of U (18·3 $\pm$ 0·4) (literature values: Pt, 21·45; U, 19·0). Determinations[19] on several samples of Pu, weighing from 4 to 28 μg, produced by reduction of PuF_4 with Ba or Mg in ThO_2 crucibles, indicated a density of 15·4 $\pm$ 0·2 g cm^{-3}. Determination on plutonium metal similarly produced in BeO crucibles[5,20] yielded consistently higher densities; these ranged 17·2 to 21·0 g cm^{-3}. With the production of larger globules of metal, the capillary pycnometers were made from regular Pyrex capillary tubing (0·2–1 mm bore) with two optically-plane surfaces parallel to each other and the axis of the tube[21] to permit precise measurement. Measurements on the mg scale confirmed the spread of densities observed earlier on the μg scale, now known to be occasioned by a spectrum of phase transformations.[2,22]

Phase transitions. The possibility of the existence of one or more allotropic modifications of plutonium metal was first suggested by ZACHARIASEN[23] who interpreted X-ray diffraction patterns of metal samples made under various conditions. This hypothesis was strengthened by the range of densities observed and by simultaneous dilatometric studies in the Metallurgical Laboratory[24] and at the Los Alamos Scientific Laboratory. Although the mg scale dilatometry represented a considerable achievement in view of the reactivity of the metal; the results obtained here as in the case of hardness and the melting point have been superseded by subsequent extensive measurements on the gram scale made at Los Alamos Scientific Laboratory[1,2,22] and Atomic Energy Research Establishment at Harwell.[25]

DISCUSSION

In the double crucible system reductions of plutonium compounds with more

[18] P. L. KIRK, R. CRAIG, J. E. GULLBERG and R. Q. BOYER *Analyt. Chem.* **19**, 427 (1947).
[19] S. FRIED and S. KATZ *Met. Lab. Report* CK–1512 (April 1944).
[20] S. KATZ *Met. Lab. Report* CK–1586 (May 1944).
[21] S. KATZ *Met. Lab. Reports:* CK–1367 (Feb. 1944); CK–1377 (Feb. 1944).
[22] E. R. JETTE *J. chem. Phys.* **23**, 365 (1955).
[23] W. H. ZACHARIASEN *Met. Lab. Reports* CK–1367 (Feb. 1944); CK–1377 (Feb. 1944).
[24] S. KATZ *Met. Lab. Report* CK–1763 (July 1944).
[25] W. B. LORD *Nature, Lond.* **173**, 534 (1954); J. G. BALL *et al. Nature, Lond.* **173**, 535 (1954).

active metals only the vapour of the reductant comes in contact with the compound to be reduced. Oxides, nitrides, etc. of the reductant are non-volatile and remain behind. The slag formed in these reactions (e.g. BaF_2, CaF_2, LiF) either soaks into the porous crucible or is volatilized at the temperature of the reaction. On a large scale (i.e. 40 mg) enough slag may be formed by reaction of the reductant with the plutonium halide that the crucible becomes "saturated." In such cases the slag appears as a glassy mass surrounding the metal globule. In any event, the maximum amount of foreign material formed adjacent to the metal is limited by the stoichiometric quantity formed by the reaction:

$$2PuF_3 + 3Ba = Pu + 3BaF_2.$$

It should be pointed out that the double crucible technique is capable of general application to the preparation of metals in this region of the periodic table and to the rare-earth metals. The new elements neptunium[26] and americium[27] and curium[28] have been prepared by this method. Protactinium though known for a long time was first prepared in a massive state by this method.[29] There is every reason to believe that as the transcurium elements become more available they too may be prepared by this method.

In the present paper we have discussed the application of this method over the range from 40 μg to 85 μg of metal. Attempts to extend the double crucible system to the gramme scale leads to difficulties from slag formation, dissipation of the heat of the highly exothermic reaction, etc. The larger scale reductions however, may have been achieved by essentially the same Goldschmidt type of reduction.[30]

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[26] S. FRIED and N. R. DAVIDSON *J. Amer. chem. Soc.* **70**, 3539 (1948).
[27] E. F. WESTRUM, JR. and L. EYRING *J. Amer. chem. Soc.* **73**, 3396 (1951).
[28] J. C. WALLMANN, W. W. T. CRANE, and B. B. CUNNINGHAM *J. Amer. chem. Soc.* **73**, 493 (1951).
[29] P. SELLERS, S. FRIED, R. ELSON and W. ZACHARIASEN *J. Amer. chem. Soc.* **76**, 5935 (1954).
[30] F. ANSELIN, P. FAUGERAS and E. GRISON *C.R. Acad. Sci., Paris* **242** 1996 (1956).

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SOME NEW TRIMERIC PHOSPHORONITRIDIC DIHALIDES

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Abstract—Three new trimeric phosphoronitridic dihalides, $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$, $P_3N_3Cl_2Br_4$, have been synthesized by the reaction of bromine-containing phosphorus halides with ammonium bromide and ammonium chloride. X-ray diffraction data, infra-red spectra and results of elemental analysis show these compounds to be trimeric, rather than tetrameric, in structure.

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THE preparation of mixtures of $(PNCl_2)_3$ and $(PNCl_2)_4$ from the reaction of phosphorus pentachloride with ammonium chloride using symmetrical tetrachloroethane as the solvent is well known.[1,2] The procedure was adapted to the preparation of $(PNBr_2)_3$ and $(PNBr_2)_4$ by the reaction of phosphorus pentabromide with ammonium bromide.[3] This procedure now has been extended to the reactions of phosphorus pentachloride with ammonium bromide and to mixtures of phosphorus pentachloride, phosphorus trichloride, phosphorus tribromide, and bromine with both ammonium chloride and bromide. As a result three new trimeric phosphoronitridic dihalides, $P_3N_3Cl_5Br$, $P_3N_3Cl_4Br_2$ and $P_3N_3Cl_2Br_4$, have been prepared. These syntheses apparently are specific for the trimeric compounds, since no tetrameric products were isolated.

DISCUSSION

1. *Syntheses*

$P_3N_3Cl_5Br$ (I). The reaction of phosphorus pentachloride with ammonium bromide produced, along with large amounts of elemental bromine, a 20 per cent yield of a white crystalline solid (I) which melted at 122·5–123·5° and was similar in properties to $(PNCl_2)_3$. An empirical formula of $P_3N_3Cl_5Br$ was indicated from the results of elemental analyses. A comparison of the infra-red spectrum of I with those of $(PNCl_2)_3$ and $(PNCl_2)_4$ indicated a trimeric structure. A molecular weight of 398 was calculated from the unit cell size (determined by X-ray diffraction) and crystal density. The theoretical molecular weight of I is 392.

Several attempts were made to determine the mode of formation of I. Although the results obtained could be used to eliminate several possible routes, a reasonable mechanism for the reaction could not be established from the available data.

It was believed at first that the reaction had occurred in two discrete steps: (1) reaction of phosphorus pentachloride with the ammonium halide to form $(PNCl_2)_3$;

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(1) R. SCHENCK and G. ROEMER *Ber. dtsch. chem. Ges.* **B57**, 1343 (1924).
(2) L. F. AUDRIETH, R. STEINMAN and A. D. F. TOY *Chem. Rev.* **32**, 109 (1943).
(3) H. BODE *Z. anorg. Chem.* **252**, 113 (1943).

(2) bromination of the $(PNCl_2)_3$ by the large amount of bromine set free during the initial stages of the reaction. This hypothesis was considered untenable when it was found that $(PNCl_2)_3$ was not brominated under similar experimental conditions.

The formation of I could be explained, however, by assuming the existence of a mixed phosphorus pentahalide containing phosphorus, chlorine, and bromine in the ratio of 3 : 14 : 1. The existence of such a phosphorus pentahalide (III) has been demonstrated[4] by the reaction of phosphorus trichloride with bromine, which afforded a product whose elemental analysis corresponded to the empirical formula $PCl_{4\cdot8}Br_{0\cdot4}$ (II). Sublimation of II at 50° gave a compound which analysed for $PCl_{4\cdot67}Br_{0\cdot33}$ (III), a yellow solid melting at 145–148°. This was shown by X-ray diffraction[4] to be a single compound of unit cell contents $P_{12}Cl_{56}Br_4$, and not a mixture of phosphorus pentahalides. In the reaction mixture from which $P_3N_3Cl_5Br$ was isolated the existence of bromine was manifest, while PCl_3 could have arisen by the reduction of PCl_5 during the oxidation of bromide to bromine. Thus III could have been the reactive species of phosphorus halide.

In this investigation attempts to prepare III by sublimation of II gave only phosphorus pentachloride. When II was allowed to react with ammonium chloride in tetrachloroethane there was obtained an 8 per cent yield of $(PNCl_2)_3$ instead of the expected I. No other crystalline product was isolated from this reaction mixture.

On the chance that the mixed phosphorus halide, III, might have formed by halogen interchange of phosphorus pentachloride with bromine, a 1 : 1 molar mixture of these two substances was allowed to react with ammonium chloride in tetrachloroethane. A 19 per cent yield of $(PNCl_2)_4$ was realized. It is interesting to note that this reaction gave only tetramer, whereas phosphorus pentachloride and ammonium chloride alone give a 3 : 1 mixture of trimer and tetramer.[1]

It is not probable that the intermediate phosphorus halide which gave rise to I was formed from the reaction of phosphorus trichloride with bromine. A reaction mixture containing ammonium bromide and a 1 : 1 molar ratio of phosphorus trichloride and bromine resulted in the formation of $P_3N_3Cl_2Br_4$(V) and not I.

These results were not sufficiently conclusive to indicate how I is formed.

$P_3N_3Cl_4Br_2$ (IV). The reaction of a 3 : 2 molar mixture of phosphorus tribromide and phosphorus pentachloride with ammonium chloride gave $P_3N_3Cl_4Br_2$ (IV), a white crystalline material melting at 132·5–135·0°. A trimeric structure was indicated by the infra-red spectrum, the results of elemental analyses and the molecular weight determination (calculated from X-ray data 433; theoretical 437).

$P_3N_3Cl_2Br_4$ (V). The reaction of a 1 : 1 molar ratio of phosphorus trichloride and bromine with ammonium bromide afforded $P_3N_3Cl_2Br_4$ (V), melting at 167·5–169·0°. The infra-red and elemental analyses indicated a trimeric structure. The molecular weight calculated from X-ray and crystal density data was 528 (theoretical = 526).

From symmetry considerations of the P_3N_3 ring, IV may exist as one or more of three geometric isomers: (a) geminal dibromide, (b) *cis*-1,3-dibromide, and (c) *trans*-1,3-dibromide. It is interesting to note that the *trans*-1,3-dibromide may exist as a pair of enantiomorphs. The same considerations apply to V. However, no indication was obtained from the X-ray data that more than one crystalline compound was isolated from each of the above reaction mixtures.

[4] A. I. Popov, D. H. Geske and N. C. Baenziger *J. Amer. chem. Soc.* **78**, 1793 (1956).

2. *X-ray diffraction studies*

All cell dimensions increase with increasing bromine content and correlate with the previously reported values for $P_3N_3Cl_6$[5] and $P_3N_3Br_6$[3]. These data are given in Table 1. All three compounds are shown to be orthorhombic by diffraction symmetry.

TABLE 1.—CRYSTAL DATA OF TRIMERIC PHOSPHORONITRIDIC DIHALIDES

Compound	*a* (*A*)	*b* (*A*)	*c* (*A*)	Volume (A^3)	Crystal *d* (obs.) g/cm³	Crystal *d* (theor.) g/cm³	Space group
$P_3N_3Cl_6$[5]	14·00	6·16	12·94	1116	1·98*	2·07	*Pnam*
$P_3N_3Cl_5Br$	14·24	6·28	13·00	1163	2·27	2·24	—
$P_3N_3Cl_4Br_2$	14·27	6·34	13·02	1178	2·44	2·46	$Pna2_1$ or *Pnam*
$P_3N_3Cl_2Br_4$	14·29	6·48	13·33	1234	2·84	2·83	—
$P_3N_3Br_6$[3]	14·38	6·64	13·35	1275	—	3·18	$Pna2_1$

* The value determined in the present investigation was 2·04.

Available data indicate the following periodic absences:

	$P_3N_3Cl_5Br$	$P_3N_3Cl_4Br_2$	$P_3N_3Cl_2Br_4$
hol	$h = 2n$	$h = 2n$	$h = 2n$
hko	?	no absences	?
okl	?	$k + 1 = 2n$	?

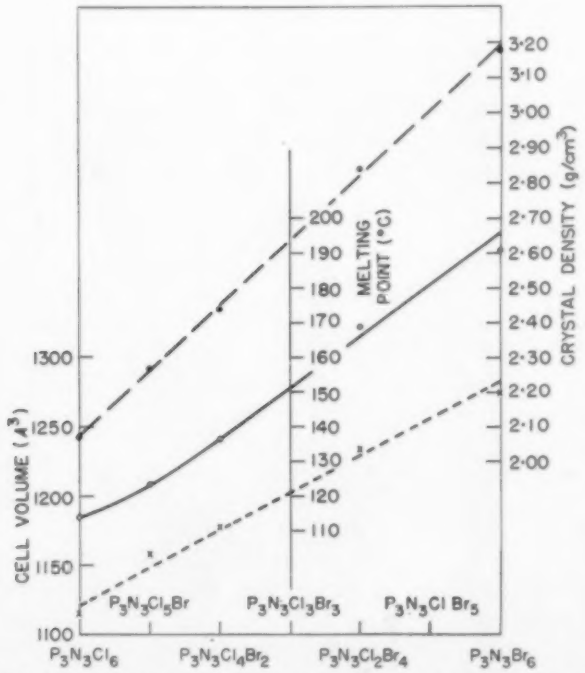

FIG. 1.—Variation of physical properties with increasing bromine substitution of $P_3N_3Cl_6$.
— — crystal density ——— melting point - - - - cell volume

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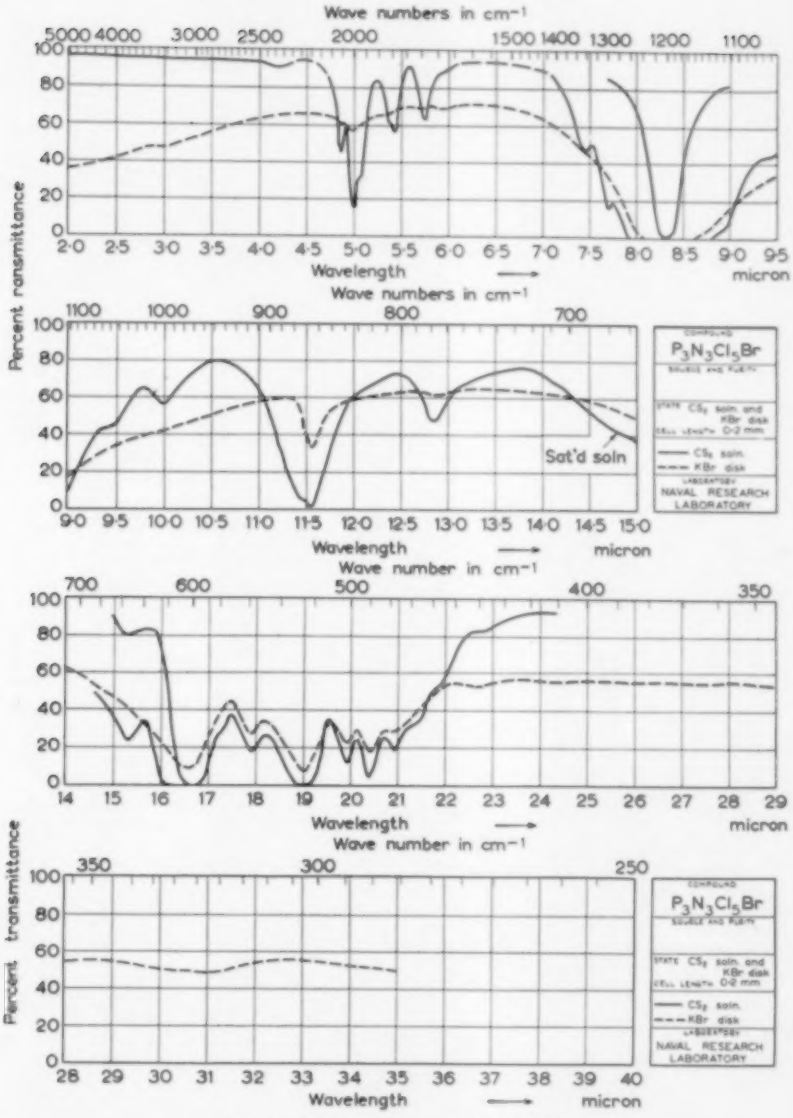
Wave numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
Percent transmittance
Wavelength → micron
2·0 2·5 3·0 3·5 4·0 4·5 5·0 5·5 6·0 6·5 7·0 7·5 8·0 8·5 9·0 9·5
Wave numbers in cm⁻¹
1100 1000 900 800 700
Sat'd soln
9·0 9·5 10·0 10·5 11·0 11·5 12·0 12·5 13·0 13·5 14·0 14·5 15·0
Wavelength → micron
P3N3Cl5Br
CS2 soln.
KBr disk
NAVAL RESEARCH LABORATORY
Wave number in cm⁻¹
700 600 500 400 350
14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29
Wavelength → micron
Wave number in cm⁻¹
350 300 250
28 29 30 31 32 33 34 35 36 37 38 39 40
Wavelength → micron
P3N3Cl5Br
CS2 soln.
KBr disk
NAVAL RESEARCH LABORATORY

FIG. 2.—Infra-red spectrum of $P_3N_3Cl_5Br$.

The similarity in cell dimensions indicate that the compounds are isostructural and the diffraction symmetry of $P_3N_3Cl_4Br_2$ indicates space groups $Pna2_1$ or $Pnam$. RENAUD[5] lists V_{2h}^{16} (or $Pnam$) for $P_3N_3Cl_6$, and BODE[3] lists C_{2v}^9 (or $Pna2_1$) for $P_3N_3Br_6$.

3. *Comparison of physical properties*

Fig. 1 shows plots of crystal density, melting point, and cell volumes against increasing bromine substitution in $(PNCl_2)_3$. An approximately linear relationship

[5] P. RENAUD *Ann. chim.* [11] **3**, 443 (1935).

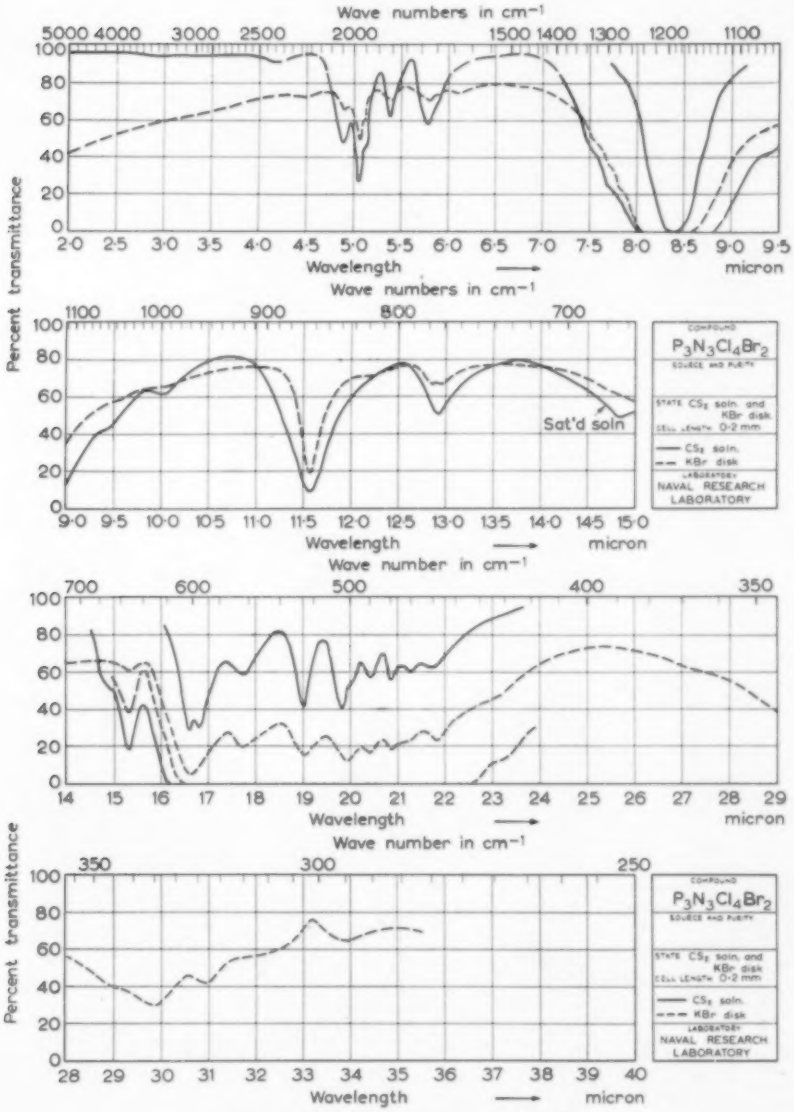

FIG. 3.—Infra-red spectrum of $P_3N_3Cl_4Br_2$.

is obtained in each case. The values of the crystal densities used are those calculated from X-ray data.

4. *Infra-red studies*

The infra-red spectra of I, IV, and V in the region from 285 to 5000 cm^{-1} are shown in Figs. 2–4. For comparison, the spectra of $(PNCl_2)_3$ and $(PNCl_2)_4$ are given in Fig. 5. The frequencies of the absorption maxima are given in Table 2.

A complete characterization of the structures of I, IV, and V from the infra-red

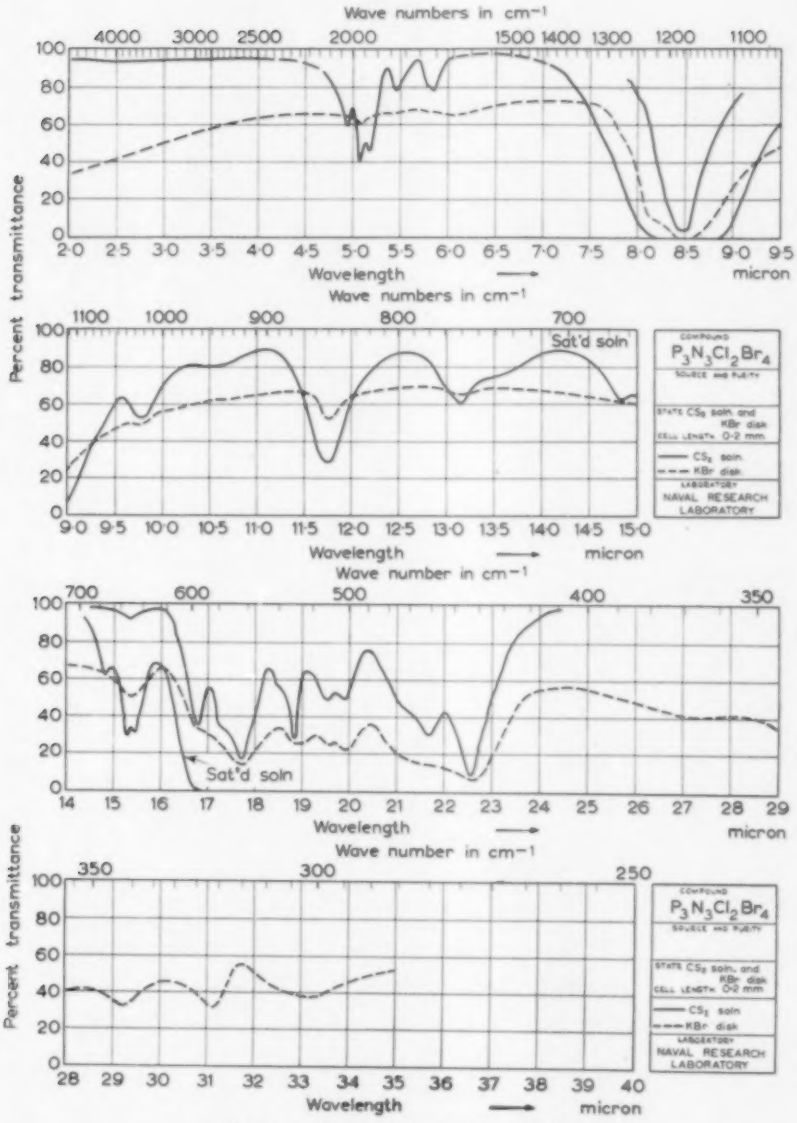

FIG. 4.—Infra-red spectrum of $P_3N_3Cl_2Br_4$.

spectra cannot be made at present since the symmetries of the brominated compounds are less than that of the parent trimer, phosphoronitridic dichloride, whose spectrum has not been explained completely.[6] However, the spectra do show some interesting correlations which, in conjunction with the other analytical data, support the formulae given above. First, the spectra of the brominated compounds and the trimer of $PNCl_2$ in the region 670–5000 cm^{-1} are similar. For example, the strong band at

[6] L. W. DAASCH *J. Amer. chem. Soc.* **76**, 3403 (1954).

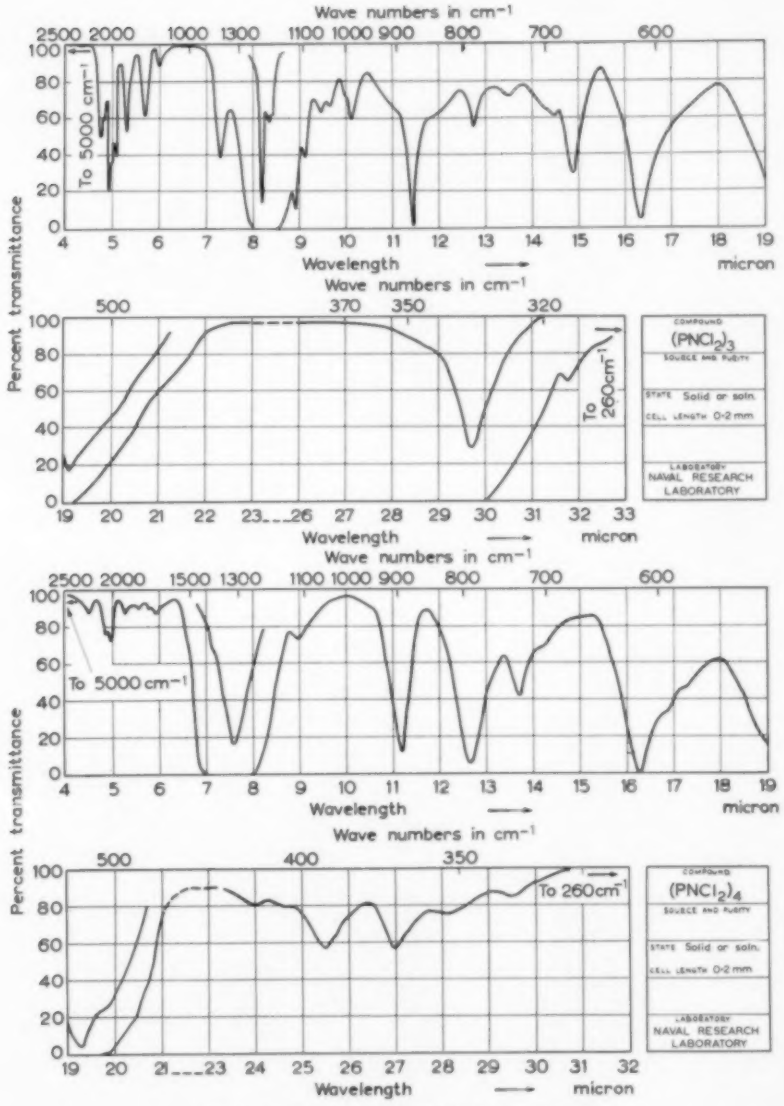

FIG. 5.—Infra-red spectra of $(PNCl_2)_3$ and $(PNCl_2)_4$.

$\sim$1200 cm^{-1} and the strong-weak relationship of the bands near 850 cm^{-1} and 760 cm^{-1} are similar to the corresponding bands in $(PNCl_2)_3$ and are thus thought to be indicative of the trimer structure as opposed to the tetramer structure. The corresponding band of higher frequency in $(PNCl_2)_4$ comes at 1315 cm^{-1}, and the 850 cm^{-1} and 760 cm^{-1} bands are of equal intensity. Although the region below 670 cm^{-1} is less helpful in this discussion, one notes that neither the brominated compounds nor $(PNCl_2)_3$ absorb in the region from 435 to 350 cm^{-1}. On the other hand, three bands appear in this region of the $(PNCl_2)_4$ spectrum. Secondly, the

TABLE 2.—FREQUENCIES OF ABSORPTION MAXIMA OF PHOSPHORONITRIDIC HALIDES (cm^{-1})

$(PNCl_2)_4$	$(PNCl_2)_3$	$P_3N_3Cl_5Br$	$P_3N_3Cl_4Br_2$	$P_3N_3Cl_3Br_4$
2200		2360	2400	
	2095			
2060	2075	2055	2048	
2020	2025	2000	1980	1960
	1975	1975	1950	1920
1860	1880	1871	1855	1837
		1865		
1700	1750	1740	1730	1725
	1660		1630	1703
	1368	1342	1335	1300
	1310	1300	1300	1240
1315 (*s*)	1218 (*s*)	1205 (*s*)	1202 (*s*)	1180 (*s*)
	1092	1060	1070	
	1040	996	1000	1021
	990	875		958
895 (*s*)	885 (*s*)	865 (*s*)	862 (*s*)	853 (*s*)
790	782	778	780	761
			772	740
730			752	
	690		672	674
	672	658	658	653
				648
615 (*s*)	612 (*s*)	608 (*s*)	602 (*s*)	
590		580	598	595
579		560	563	575
				568
				541
				532
520 (*s*)	522 (*s*)	527 (*s*)	528	516
512		505	508	503
			500	
		490	489	
		478	481	475
		467	469	463
		440	461	443
393			435	
370			345	369 (*vw*)
355			335	342
339	336	325	327	322
	315		310	303
			296	

(*s*) denotes strong absorption band.
(*vw*) denotes very weak absorption band.

gradual shift to lower frequencies of most of the bands in the 670–5000 cm^{-1} region is explained by the substitution of the heavier bromine atoms for chlorine.

Table 2 is arranged so that corresponding frequencies in the various compounds are listed in a horizontal row. The fact that all the brominated products show several absorption bands in the region from 435 to 500 cm^{-1}, where $(PNCl_2)_3$ and $(PNCl_2)_4$ have no absorption would indicate that this range probably contains absorption due to the stretching vibration of PBr and PBr_2 groups.

The spectra of the brominated products give some additional support to and information as to the vibrational assignments[6] of some of the bands in $(PNCl_2)_3$. It is fairly certain now that the bands at 1218 cm^{-1} and 885 cm^{-1} in $(PNCl_2)_3$ are ring vibrations which are not materially affected by substitutions on the phosphorus atoms, that is, they arise from vibrations which characterize the P_3N_3 ring. The band near 522 cm^{-1} is less characteristic of the ring since it is not as apparent in $P_3N_3Cl_2Br_4$ as in the other derivatives. The normal mode for this vibration probably contains a mixture of ring and PCl_2 vibrations.

EXPERIMENTAL

Reagents. All chemicals used were reagent grade. Phosphorus halides, bromine and benzene were used without further purification. The ammonium halides were dried for 12 hr at 105°. Symmetrical tetrachloroethane was distilled and stored over Drierite.

X-ray diffraction measurements. The cell dimensions were obtained by single crystal measurements using the Weissenberg method. All measurements were made on crystals rotated about the "*b*" axis. Values of "*b*" were obtained from oscillation photographs, and "*a*" and "*c*" from zero layer Weissenberg diagrams. A first layer diagram was obtained for $P_3N_3Cl_4Br_2$.

Infra-red measurements. The spectra in the 670–5000 cm^{-1} range were obtained with a Perkin-Elmer model 21 infra-red spectrophotometer equipped with sodium chloride optics. A model 112 double pass spectrophotometer with potassium bromide or caesium bromide prisms was used for the 285–670 cm^{-1} region. The carbon disulphide solutions were contained in a conventional liquid cell having a thickness of 0·2 mm. The potassium bromide disks were prepared in the standard manner.

Synthesis of $P_3N_3Cl_5Br$ (I). The procedure used was essentially that of SCHENCK and ROEMER,[1] except that ammonium bromide replaced the ammonium chloride. A stirred mixture of 453·6 g (2·18 moles) of phosphorus pentachloride, 427·0 g (4·36 moles) of ammonium bromide, and 1300 ml of tetrachloroethane was heated slowly to reflux under a condenser fitted with a Drierite-filled column connected to a funnel inverted over a water-bath. Evolution of hydrogen halide began at a pot temperature of about 110°. Bromine evolution was strong throughout the earlier periods of heating. Refluxing and stirring were continued for a total of 20 hr, at which time the evolution of hydrogen halide and bromine had ceased.

When cool, the mixture was filtered and the solid washed with tetrachlorethane, then absolute ether, and dried. There was obtained 250·2 g of mixed ammonium halides. The presence of both bromide and chloride was demonstrated by standard qualitative tests.

The combined tetrachloroethane filtrates were concentrated *in vacuo* at less than 100°. After about one-fourth of the solvent had been distilled a solid began to

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separate in the pot. The distillation was interrupted and the pot mixture was chilled and filtered to obtain 14·8 g of a light yellow solid (VI), which softened at 126°, then melted at 130–132°. Exposure to the atmosphere resulted in extensive decomposition, with the evolution of hydrogen chloride and bromine. A syrupy liquid remained. When VI was stirred and refluxed in tetrachloroethane with an excess of ammonium chloride, no evolution of hydrogen halide was observed. From this it may be concluded that the yellow solid VI is a by-product of the reaction and not an intermediate.

The filtrate was returned to the pot and concentration was continued until the total volume was 100–200 ml. This residue was chilled, the resulting mixture was filtered, the solid washed twice with water, and then crystallized three times from benzene. There was obtained 57·80 g of $P_3N_3Cl_5Br$ (I), as white prisms, m.p. 120·0–123·0°, which resembled $(PNCl_2)_3$. An analytical sample melted at 122·5–123·5°. The crystal density was 2·27 g/cm³. (Found: P, 22·75 (average of 6 determinations); N, 10·20, 9·93; Cl, 44·97, 45·14; Br, 20·47, 20·56. Calc. for $P_3N_3Cl_5Br$: P, 23·70; N, 10·71; Cl, 45·21; Br, 20·38.)*

Synthesis of $P_3N_3Cl_4Br_2$ (IV). To a mixture of 44·8 g (0·215 mole) of phosphorus pentachloride, 150 ml of tetrachloroethane, and 23·0 g (0·43 mole) of ammonium chloride, was added 87·5 g (0·325 mole) of phosphorus tribromide. This was heated slowly to reflux, then stirred and refluxed for a total of 24 hr. Hydrogen halide evolution began at 99°. Following the isolation procedure described above there was obtained 3·79 g of $P_3N_3Cl_4Br_2$ (IV), white prisms melting at 132·5–135·0°, after crystallization from benzene. An analytical sample melted at 134·5–136·5°. The crystal density was 2·44 g/cm³. (Found: P, 19·72, 19·99; N, 9·40, 9·32; Cl, 32·09, 32·09; Br, 36·30, 36·19. Calc. for $P_3N_3Cl_4Br_2$: P, 21·29; N, 9·62; Cl, 32·48; Br, 36·61.)

No yellow solid analogous to VI was obtained on partial evaporation of the filtrate.

Synthesis of $P_3N_3Cl_2Br_4$ (V). To a stirred mixture of 107 g (1·09 moles) of ammonium bromide, 350 ml of tetrachloroethane, and 74·86 g (0·545 mole) of phosphorus trichloride, was added 87·11 g (0·545 mole) of bromide. The mixture was heated slowly to reflux then stirred and refluxed for a total of 27 hr. Evolution of hydrogen halide was observed to begin at 86°. Following the usual isolation procedure there was obtained 68·3 g of a mixture of ammonium halides, 2·36 g of a yellow solid analogous to VI, and finally, 21·81 g of $P_3N_3Cl_2Br_4$ (V), white prisms, m.p. 165·5–167·0° after crystallization from benzene. The crystal density was 2·84 g/cm³. (Found: P, 16·59 (average of 4 determinations); N, 7·82, 8·12; Cl, 13·31, 13·52; Br, 59·31, 59·52. Calc. for $P_3N_3Cl_2Br_4$; P, 17·68; N, 8·00; Cl, 13·49; Br, 60·82.)

Attempted bromination of $(PNCl_2)_3$. A solution of 21·0 g of $(PNCl_2)_3$, 200 ml of tetrachloroethane, and 9·7 g of bromine was stirred and heated 20 hr at 120–130°. This was then concentrated *in vacuo* to about 50 ml whereupon 14·3 g (68 per cent recovery) of $(PNCl_2)_3$ was obtained. A mixture with an authentic sample of $(PNCl_2)_3$ showed no depression in melting point. This compound was not isolated at this point of the synthesis of $P_3N_3Cl_5Br$.

* Analyses by Oakwold Laboratories, Alexandria, Virginia, and Prof. M. Kathryn Gerdeman and Miss Jane R. Swan of the University of Maryland, College Park, Maryland. Melting points are corrected. Crystal densities were determined by the flotation method using aqueous lead perchlorate solutions.

Reaction of $PCl_{4\cdot8}Br_{0\cdot4}$ *with* NH_4Cl. A mixture of 14·6 g (0·0625 mole) of $PCl_{4\cdot8}Br_{4\cdot8}$ (prepared by the method of POPOV, GESKE, and BAENZIGER,[4] 6·70 g (0·125 mole) of ammonium chloride, and 100 ml of tetrachloroethane was stirred and refluxed 4 hr. Hydrogen halide evolution began at 130°. Following the usual isolation procedure there was obtained 0·55 g of $(PNCl_2)_3$. A mixture of this compound with an authentic sample of $(PNCl_2)_3$ showed no depression in melting point.

Reaction of a 1 : 1 *Mixture of* PCl_5 *and* Br_2 *with* NH_4Cl. A stirred mixture of 89·6 g (0·43 mole) of phosphorus pentachloride, 46·0 g (0·86 mole) of ammonium chloride, 200 ml of tetrachloroethane, and 68·7 g (0·43 mole) of bromine was stirred and heated to reflux. Hydrogen halide evolution was rapid at 98°. Stirring and refluxing were continued for 22 hr, after which time there was obtained 9·67 g (19 per cent yield based on the weight of PCl_5) of $(PNCl_2)_4$. A mixture of this compound with I melted at 92–112°, whereas a mixture with an authentic sample of $(PNCl_2)_4$ showed no depression of melting point.

Phosphorus analyses. The reason why the brominated compounds (I, IV, and V) all analysed low in phosphorus is not apparent. The analytical procedure used involved decomposition of the sample with nitric-sulphuric acid, followed by precipitation of the phosphorus with ammonium molybdate. After low results were obtained on compound V by two independent laboratories, a sample was decomposed by fusion with a mixture of sodium peroxide, potassium nitrate and trinitrobenzene in a Parr bomb. Results were again low by the same amount. A pure sample of $(PNCl_2)_3$ was then analysed by both laboratories using the acid decomposition method. These analyses agreed well with the theoretical value.

Acknowledgement—The authors are grateful to Mr. HERBERT T. SIMMONS of the Explosives Research Department, U.S. Naval Ordnance Laboratory, for the crystal density measurements.

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REACTIONS OF CHLOROSILANES WITH FORMALDEHYDE—I

CHLOROMETHOXYTRICHLOROSILANE AND ITS DECOMPOSITION

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(*Received* 1 *April* 1957)

Abstract—Chloromethoxytrichlorosilane, $ClCH_2OSiCl_3$, was prepared both by chlorination of methoxytrichlorosilane and by the reaction of silicon tetrachloride with formaldehyde. Chloromethoxydichlorosilane, $ClCH_2OSiHCl_2$, similarly was obtained as the product of the reaction of trichlorosilane with formaldehyde. The least stable chloromethoxysilane was found to be $ClCH_2OSiH_3$, which decomposed rapidly to monochlorosilane and formaldehyde at room temperature, and the most stable was $ClCH_2OSiCl_3$, which on standing at room temperature slowly reverted to silicon tetrachloride and a non-volatile liquid, probably bis(chloromethoxy)dichlorosilane. At elevated temperature the decomposition of chloromethoxytrichlorosilane to silicon tetrachloride and formaldehyde was brought to completion by the decomposition of formaldehyde to hydrogen, carbon monoxide, and methanol. Chloromethoxytrichlorosilane readily reacted with aluminium chloride at 150° to form methylene chloride and a non-volatile product which contained alumino-chlorosilicates.

THE possibility of reaction between a silicon–chlorine link and the carbonyl group of an aldehyde has been recognized recently by several investigators. Although ROCHOW and GINGOLD[1] were unable to detect any reaction between benzaldehyde and chlorosilanes, even after the reactants had been refluxed together for 4 days, ZAPPEL[2] has reported that at room temperature a slow reaction between benzaldehyde and silicon tetrachloride leads to the formation of chloropolysiloxanes and benzal chloride. It has been suggested that this reaction proceeds in two stages: (1) addition of the silicon–chlorine link to the carbonyl of benzaldehyde

$$SiCl_4 + C_6H_5CHO \longrightarrow C_6H_5CHClOSiCl_3$$

and (2) reaction of the product with a further silicon–chlorine link:

$$C_6H_5CHClOSiCl_3 + \equiv Si{-}Cl \longrightarrow C_6H_5CHCl_2 + \equiv SiOSiCl_3$$

Since no products from equation (1) were found among the products of the reaction, it was reasoned that reaction (2) proceeds relatively rapidly.

1-Chloroalkoxychlorosilanes have been prepared recently by BREEDERVELD and WATERMAN[3] by the chlorination of alkoxychlorosilanes. In this way, they prepared chloromethoxytrichlorosilane and 1-chloroethoxytrichlorosilane from the corresponding methoxy- and ethoxytrichlorosilanes. Their attempt to prepare 1-chloroethoxytrichlorosilane by the reaction of acetaldehyde, silicon tetrachloride, and hydrogen chloride resulted, instead, in the formation of bis(chloromethyl) ether and silica:

$$2CH_3CHO + 2HCl \longrightarrow CH_3CHClOCHClCH_3 + H_2O$$

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

[1] E. G. ROCHOW and K. GINGOLD *J. Amer. chem. Soc.* **76**, 4852 (1954).
[2] A. ZAPPEL *J. Amer. chem. Soc.* **77**, 4228 (1955).
[3] H. BREEDERVELD and H. I. WATERMAN Research Correspondence, Supplement to *Research* Lond. **7**, No. 2, 12 (1954).

4 (20 pp.)

We have investigated the vapour-phase reactions of chlorosilanes with formaldehyde, and have studied particularly the properties and reactions of chloromethoxytrichlorosilane.

EXPERIMENTAL

Preparation of chloromethoxytrichlorosilane by chlorination of methoxytrichlorosilane

A three-neck, 100 cm³, round-bottom flask was fitted with a gas inlet tube and a thermometer well. A 40 cm Pyrex tube with an inside diameter of 20 mm, a water-cooled reflux condenser, and a dry-ice condenser were connected to the remaining neck of the flask in that order. The Pyrex tube was irradiated with a General Electric 15 W germicidal lamp. Nitrogen was led past the outlet of the dry-ice condenser through a T-tube and into a bubbler.

After the apparatus was swept with nitrogen, 53·9 g of methoxytrichlorosilane was placed in the flask and brought to reflux. A solution containing an amount of sodium hydroxide equivalent to the amount of hydrogen chloride expected to result from monochlorination of the methoxytrichlorosilane was placed in the bubbler with bromcresol green indicator. Chlorine was passed slowly into the flask for 7 hr, during which time the temperature of the refluxing material rose from 81 to 123°C. Change in the colour of the indicator indicated completion of the reaction. Fractionation of the product in a precision column gave 46·8 g (70·4 per cent yield) of chloromethoxytrichlorosilane, b.p. 123·5°C, μ_D^{20} 1·4333*(Found: C, 6·00; H, 1·39; Si, 14·21; Cl, 70·06. Calc. for $ClCH_2OSiCl_3$: C, 6·01; H, 1·01; Si, 14·04; Cl, 70·95%).

Saturation vapour pressures of a freshly distilled sample of chloromethoxytrichlorosilane were measured in a tensimeter[4] in a vacuum system of conventional design. Temperatures were read on a certified mercury thermometer.

VAPOUR PRESSURES OF LIQUID $ClCH_2OSiCl_3$

t (°C)	0·0	10·0	20·0	30·0	40·0	50·0
P_{mm} (obs.)	3·10	5·82	10·7	18·9	32·0	51·8
P_{mm} (calc.)	3·07	5·83	10·6	18·6	31·3	51·4

The observed vapour pressures fit the equation

$$\log_{10} P_{mm} = 8{\cdot}395 - 2159/T$$

A melting range of −147 to −145°C (measured with an ethylene vapour-pressure thermometer) was determined (Stock magnetic plunger method) for the sample of chloromethoxytrichlorosilane after it had been used in the tensimeter. The infra-red absorption spectrum of the vapour (Fig. 1) was recorded, using a Perkin-Elmer Model 21 double-beam spectrophotometer and a gas cell with a path length of 4 cm.

Thermal decomposition of chloromethoxytrichlorosilane

A 4·301 g (21·5 millimole) sample of chloromethoxytrichlorosilane was heated at 400°C for 12 hr in a sealed 1·4 l. Pyrex tube. In addition to a large amount of material which was not condensable at −196°C, the product of the pyrolysis included condensable materials which were separated in a vacuum apparatus. The identities of the condensable products were established by their volatilities and infra-red spectra, confirmation of each identification being obtained by measurement of molecular weights. The condensable products contained 90·6 cm³† (4·04 millimole) of hydrogen chloride, 5·2 cm³ (0·23 millimole) of carbon dioxide (the mixture of hydrogen chloride and carbon dioxide was dissolved in aqueous alkali, and the solution was acidified and titrated potentiometrically with silver nitrate), 4·8 cm³ (0·21 millimole) of methyl chloride (mol. wt. found 50·0, calc. 50·5), 3·477 g of a mixture of silicon tetrachloride (mol. wt. found 170, calc. 170), and methoxytrichlorosilane (mol. wt. found 164, calc. 165·5), and 0·067 g (0·24 millimole) of hexachlorodisiloxane (mol. wt. found 258, calc. 285). A 26·3-cm³ sample of the non-condensable product

* Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

† Unless otherwise qualified, cm³ refers to volume at standard temperature and pressure.

[4] A. B. BURG and H. I. SCHLESINGER *J. Amer. chem. Soc.* **59**, 780 (1937).

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was burned over copper (II) oxide at 700°C to give 14·4 cm³ of a gas which was condensable at −196°C but non-condensable at −78°C (mol. wt. found 44, calc. for CO_2, 44). The non-condensable product thus consisted of carbon monoxide and hydrogen in the ratio of 1·21 to 1·00.

Reaction of chloromethoxytrichlorosilane with aluminium chloride

In a sealed Pyrex bulb with a volume of 300 cm³, 0·324 g of freshly sublimed aluminium chloride and 1·406 g (7·03 millimole) of chloromethoxytrichlorosilane were allowed to react at 150°C for 12 hr. The products of the reaction included 2·49 cm³ (0·11 millimole) of hydrogen chloride (mol. wt. found 36 ± 1, calc. 36·5), 1·24 cm³ (0·05 millimole) of methyl chloride (mol. wt. found 52 ± 2, calc. 50·5), 0·558 g (6·73 millimole) of methylene chloride (mol. wt. found 85·8, calc. 85), 0·105 g (0·53 millimole) of silicon tetrachloride, 0·0427 g (1·5 millimole) of hexachlorodisiloxane (mol. wt. found 259 ± 4, calc. 285), and 1·036 g of non-volatile residue.

Reaction of silicon tetrachloride with formaldehyde

Anhydrous formaldehyde was obtained by phosphoric acid-catalysed depolymerization of trioxane vapour in a stream of nitrogen.[5] Formaldehyde was removed from the stream by condensation in a trap at −78°C, and was purified by distillation in a slow stream of nitrogen into a second trap at −78°C.

A small glass ampoule, one end of which was blown to a thin-walled bulb, was filled in vacuum with 4·016 g (23·6 millimole) of silicon tetrachloride and sealed. The ampoule was placed in a 1·7 l. Pyrex tube which was then evacuated, filled with 262 cm³ (17·7 millimole) of formaldehyde, and sealed. When the temperature of the reaction tube was raised to 200°C, the tube was shaken, thus exploding the ampoule and mixing the reactants as gases. The reaction was allowed to continue at 200°C for 24 hr. The products of the reaction included 3·0 cm³ of hydrogen chloride, 1·0 cm³ of an unidentified material which was condensable at −140°C but non-condensable at −100°C, 3·346 g of silicon tetrachloride, and 0·478 g (10 per cent yield) of chloromethoxytrichlorosilane (identified by its infra-red absorption spectrum). The chloromethoxytrichlorosilane contained a trace of trioxane which could not be removed by bulb-to-bulb distillation in the vacuum apparatus.

When 4·350 g (25·6 millimole) of silicon tetrachloride and 282 cm³ (12·6 millimole) of formaldehyde were frozen together into the cold finger of a 1·4 l. Pyrex tube and allowed to react at 200°C for 24 hr, the products obtained included 1·9 cm³ of hydrogen chloride, 3·508 g of silicon tetrachloride, 0·484 g (9·5 per cent yield) of chloromethoxytrichlorosilane, and a non-volatile liquid which apparently was obscured by powdered glass in the first experiment. The non-volatile product readily hydrolysed to hydrogen chloride, formaldehyde, and silica, and the similarity of its infra-red absorption spectrum to that of chloromethoxytrichlorosilane (both in CS_2) suggested that the non-volatile material consisted, at least partly, of bis- or poly(chloromethoxy)chlorosilanes.

Formation of chloromethoxydichlorosilane by the reaction of trichlorosilane with formaldehyde

In a Pyrex reaction tube with a volume of 1·4 l., 443 cm³ (19·8 millimole) of trichlorosilane and 222 cm³ (9·9 millimole) of formaldehyde were allowed to react at 200°C for 24 hr. Products of the reaction included 342 cm³ of trichlorosilane, 0·536 g (16 per cent yield) of chloromethoxydichlorosilane (mol. wt. found 166, calc. 166·5), and approximately 0·2 ml of a non-volatile liquid. The infra-red absorption spectrum of the vapour of chloromethoxydichlorosilane is given in Fig. 2.

Reactions of mono- and di-chlorosilane with formaldehyde

In a Pyrex bulb with a volume of 300 cm³, 101 cm³ (4·5 millimole) of monochlorosilane and 77 cm³ (3·4 millimole) of formaldehyde were allowed to react at 200°C for 19·5 hr. The product of the reaction was examined immediately. By repeated passage of the product through a trap at −112°C there was obtained 66·2 cm³ of monochlorosilane (mol. wt. found 66·8, calc. 66·5), which was not condensable at −112°C. The material retained in the trap at −112°C contained formaldehyde and a material which was believed to be chloromethoxysilane on the basis of certain aspects of its infra-red absorption spectrum, particularly a strong absorption at 1150–1130 cm.$^{-1}$ The decomposition of

[5] A. W. Schnitzer, G. J. Fisher and A. F. Maclean *J. Amer. chem. Soc.* **75**, 4347 (1953).

chloromethoxysilane appeared to be fairly rapid, since the absorption at 1150–1130 cm^{-1} decreased to about one-third of its initial value in 50 min. At the same time the intensity of bands associated with formaldehyde increased.

After 103 cm^3 (4·6 millimole) of dichlorosilane and 75·6 cm^3 (3·4 millimole) of formaldehyde were allowed to react at 200°C for 19 hr, 39 cm^3 of the dichlorosilane was recovered, and the product contained a material, probably chloromethoxydichlorosilane, which absorbed strongly at 1133 cm^{-1}.

Decomposition of chloromethoxytrichlorosilane and chloromethoxydichlorosilane at room temperature

Chloromethoxytrichlorosilane and chloromethoxydichlorosilane which had been prepared by reaction of formaldehyde with the corresponding chlorosilane were sealed separately into Pyrex ampoules. After 3 months 0·484 g (2·42 millimole) of chloromethoxytrichlorosilane had decomposed to 2·2 cm^3 of hydrogen chloride (mol. wt. found 36 ± 1, calc. 36·5), 10·9 cm^3 (0·49 millimole) of silicon tetrachloride (mol. wt. found 169, calc. 170), 0·338 g (1·69 millimole) of chloromethoxytrichlorosilane, and a non-volatile material which appeared to be identical to the non-volatile material which was obtained in the reaction of silicon tetrachloride with formaldehyde. After 2 months 0·536 g (3·22 millimole) of chloromethoxydichlorosilane had decomposed to 1·0 cm^3 of hydrogen chloride, 16·1 cm^3 (0·72 millimole) of trichlorosilane (mol. wt. found 134, calc. 134·5), 0·338 g (2·04 millimole) of chloromethoxydichlorosilane (mol. wt. found 164, calc. 166·5), and a non-volatile material which appeared to be identical to the non-volatile material which was obtained in the reaction of trichlorosilane with formaldehyde.

DISCUSSION

The chlorination of methoxytrichlorosilane which was carried out here in the vapour-phase in ultra-violet light gave a considerably better yield (70 per cent) of chloromethoxytrichlorosilane than was obtained (20 per cent) by BREEDERVELD and WATERMAN[3] by chlorination of methoxytrichlorosilane in diffuse daylight.

Chloromethoxytrichlorosilane was found to decompose thermally to silicon tetrachloride and formaldehyde. At 400°C this decomposition was brought to completion by the further decomposition of formaldehyde to hydrogen, carbon monoxide, carbon dioxide, and methanol. Reaction of methanol with silicon tetrachloride accounts for the formation of methoxytrichlorosilane and for the formation of most of the hydrogen chloride which was obtained.

$$ClCH_2OSiCl_3 \xrightarrow{\Delta} SiCl_4 + CH_2O$$

$$CH_2O \xrightarrow{\Delta} H_2 + CO$$

$$2CH_2O \xrightarrow{\Delta} 2H_2 + CO_2 + C$$

$$2CH_2O \xrightarrow{\Delta} CH_3OH + CO$$

$$CH_3OH + SiCl_4 \longrightarrow HCl + CH_3OSiCl_3$$

The small amounts of methyl chloride and hexachlorodisiloxane which were obtained probably arose from the reaction of methanol with hydrogen chloride:

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

$$2SiCl_4 + H_2O \longrightarrow Cl_6Si_2O + 2HCl$$

or from the reaction of hydrogen chloride with formaldehyde:

$$2CH_2O + 2HCl \longrightarrow ClCH_2OCH_2Cl + H_2O$$

$$2SiCl_4 + H_2O \longrightarrow Cl_6Si_2O + 2HCl$$

$$ClCH_2OCH_2Cl \xrightarrow{\Delta} CH_3Cl + HCl + CO$$

Chloromethoxytrichlorosilane and chloromethoxydichlorosilane also apparently underwent rearrangement on standing at room temperature:

$$2\ ClCH_2OSiCl_3 \longrightarrow SiCl_4 + (ClCH_2O)_2SiCl_2$$

$$2\ ClCH_2OSiHCl_2 \longrightarrow SiHCl_3 + (ClCH_2O)_2SiHCl$$

A sample of chloromethoxytrichlorosilane underwent 20 per cent rearrangement in 3 months, while a sample of chloromethoxydichlorosilane underwent 22 per cent rearrangement in 2 months.

The formation of chloromethoxytrichlorosilane by the reaction of silicon tetrachloride with formaldehyde and the formation of chloromethoxydichlorosilane by the reaction of trichlorosilane with formaldehyde are the first definite examples of addition of silicon–chlorine bonds to the carbonyl group of an aldehyde:

$$SiCl_4 + CH_2O \longrightarrow ClCH_2OSiCl_3$$

$$SiHCl_3 + CH_2O \longrightarrow ClCH_2OSiHCl_2$$

ZAPPEL[2] has suggested that a similar reaction occurs between silicon tetrachloride and benzaldehyde, but his suggestion that the phenylchloromethoxychlorosilanes so formed react further with silicon–chlorine bonds to form benzal chloride and chlorosiloxanes is not consistent with the reactions of chloromethoxytrichlorosilane which were studied here. Chloromethoxytrichlorosilane does not react with silicon–chlorine bonds either at elevated temperature or on standing at room temperature. Although the reactivity of phenylchloromethoxychlorosilanes might differ from that of chloromethoxychlorosilanes, it should be pointed out that the reaction of silicon tetrachloride with benzaldehyde to form benzal chloride and chlorosiloxanes is similar to the reactions of chloro- and nitro-substituted benzaldehydes which form chloro- and nitrobenzal chloride in the presence of phosphorus pentachloride. Bis(chloro- and nitrophenylchloromethyl) ethers have been isolated as intermediate products in these reactions.[6,7]

Although no reaction was found to occur between chloromethoxytrichlorosilane and silicon–chlorine bonds, chloromethoxytrichlorosilane reacted readily with aluminium chloride 150°C to form methylene chloride and a non-volatile material which probably contained aluminochlorosilicates. When the weight of the non-volatile product, excluding the weight of aluminium chloride which was introduced into the reaction, was considered to be (Cl_2SiO), 100 per cent of the silicon and chlorine entering reaction as chloromethoxytrichlorosilane could be accounted for in the volatile and non-volatile products:

$$ClCH_2OSiCl_3 + AlCl_3 \longrightarrow CH_2Cl_2 + Cl_2AlOSiCl_3$$

Additional reactions must have occurred, since the amount of (Cl_2SiO) formed (6·20 millimole) was less than that which would be expected from the amount of methylene chloride obtained (6·73 millimole), and since silicon tetrachloride and small amounts of methyl chloride and hexachlorodisiloxane also were obtained. The amount of silicon tetrachloride obtained (0·53 millimole) corresponded to the amount of methylene chloride formed in excess of the amount of (Cl_2SiO) obtained, and it is likely that in

[6] S. C. J. OLIVIER and A. P. WEBER *Rec. trav. chim.* **52,** 169 (1933).
[7] A. KLIEGEL *Ber. dtsch. chem. Ges.* **40,** 4937 (1907).

addition to reaction with aluminium chloride chloromethoxytrichlorosilane decomposed to silicon tetrachloride and formaldehyde, and that the formaldehyde reacted with aluminium chloride to form methylene chloride.

Certain well-characterized bands can be distinguished in the infra-red absorption spectra of chloromethoxychlorosilanes. The strong absorption in the region of 1150 to 1100 cm^{-1} undoubtedly is associated with the stretching vibrations of the C—O—Si bonds. The weak absorptions at 2950 cm^{-1} and 2880 cm^{-1} are associated with the carbon–hydrogen stretching vibrations of the methylene group. In chloromethoxydichlorosilane the silicon–hydrogen stretching vibration gives rise to the absorption at 2245 $cm.^{-1}$ Carbon–chlorine stretching vibrations account for the absorption at 722 cm^{-1} in the spectrum of chloromethoxytrichlorosilane and for the absorption at 713 cm^{-1} in the spectrum of chloromethoxydichlorosilane.

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REACTIONS OF CHLOROSILANES WITH FORMALDEHYDE—II

REACTION OF SILICON TETRACHLORIDE WITH FORMALDEHYDE OVER ALUMINA

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Abstract—Passage of a mixture of silicon tetrachloride and formaldehyde over activated alumina at 400°C gave principally hydrogen chloride, methyl chloride, and chlorosiloxanes or silica, plus small amounts of methylene chloride. Chlorosilanes, which had been reported to be the product of the reaction of silicon tetrachloride with decomposing formaldehyde over activated alumina, were not obtained. Chloromethoxytrichlorosilane, $ClCH_2OSiCl_3$, may well have been an intermediate product in the present reaction because passage of its vapour over alumina at 200°C gave the same products (hydrogen chloride, methyl chloride, methylene chloride, silicon tetrachloride, and a nonvolatile material with an empirical composition Cl_2SiO) in the same proportions.

ALTHOUGH chlorosilanes can be reduced cleanly to silanes by the action of lithium aluminium hydride in ether solution,[1] some other method involving a more common reducing reagent would be desirable, especially if a considerable quantity of the chlorosilane were to be reduced. In this laboratory the vapour-phase reaction of methyltrichlorosilane with hydrogen sulphide and related compounds was investigated,[2] but no reduction resulted. The report by GLEMSER and LOHMAN[3] that passage of the vapours of silicon tetrachloride and formaldehyde over alumina at 350–500°C yields mono- and di-chlorosilane therefore was encouraging. At 400°C and using a ratio of silicon tetrachloride to formaldehyde of 1 : 3 an almost quantitative transformation of silicon tetrachloride was claimed, giving mono- and di-chlorosilane in 86 and 13·2 per cent yield respectively. The compounds were separated by distillation in a vacuum system and were identified only by their vapour tensions. It was assumed that formaldehyde decomposes to carbon monoxide and hydrogen at the stated temperature, and was postulated that in the presence of the catalyst atomic hydrogen reacts with silicon tetrachloride to form hydrogen chloride and chlorosilane radicals, the latter then reacting further with hydrogen atoms to give chlorosilanes:

$$SiCl_4 + 2H \longrightarrow SiCl_2 + 2HCl$$

$$SiCl_2 + 2H \longrightarrow SiH_2Cl_2$$

Using a similar technique, we attempted the synthesis of organochlorosilanes of

[1] A. E. FINHOLT, A. C. BOND, JR., K. E. WITZBACH and H. I. SCHLESINGER *J. Amer. chem. Soc.* **69**, 2692 (1947).
[2] Unpublished work at Harvard University.
[3] O. GLEMSER and W. LOHMANN *Z. anorg. Chem.* **275**, 260 (1954).

the type $CH_3SiH_xCl_{3-x}$ from methyltrichlorosilane and formaldehyde. A study of the infra-red absorption spectra of the products revealed that none showed bands in the range 2300–2100 cm^{-1}, the region of absorption of the silicon–hydrogen link.[4] This prompted us to reinvestigate the silicon tetrachloride–formaldehyde reaction with the alumina catalysts at our disposal.

EXPERIMENTAL

Monomeric formaldehyde. Monomeric formaldehyde was obtained by phosphoric acid-catalysed depolymerization of trioxane vapour in a stream of nitrogen,[5] and was used directly from the generator.

Activated alumina. Experiments were performed using alumina from several sources. Before use, the aluminas were ignited for 3–4 hr at 650°C; they were used directly or were cooled and stored in a desiccator over phosphorus pentoxide. After activation, the aluminas still contained considerable amounts of water which could not be expelled even by heating for 24 hr *in vacuo*. Water which could not be expelled by heating was displaced from the alumina before a reaction was begun by sweeping the alumina with hydrogen chloride or with silicon tetrachloride in a stream of nitrogen. Merck (U.S.A.) and Mallinckrodt alumina powders were supported on Pyrex wool; Aluminum Company of America F-1 activated alumina (1/4 in. spheres) required no support.

Reaction of silicon tetrachloride with formaldehyde over alumina at 400°C. The following experiment is typical of a large number of reactions between silicon tetrachloride and formaldehyde which were carried out using various proportions of the reactants over several alumina catalysts at temperatures ranging from 325 to 425°C:

Aluminum Company of America F-1 activated alumina (1/4 in.) was ignited as above and then poured directly into a tared Pyrex tube with an inside diameter of 20 mm. The temperature of the alumina was adjusted to 400°C; and the alumina was swept with silicon tetrachloride in a stream of nitrogen until water no longer condensed from the exit gases when they were passed through a cooled tube. The silicon tetrachloride-swept catalyst then was swept with dry nitrogen for 12 hr, cooled in a stream of nitrogen, and the tube and catalyst re-weighed. A sample of swept catalyst was removed; 51·56 g of catalyst remained as a packing 24·5 cm in length. The sample of swept catalyst was treated with a 0·1 M solution of sodium hydroxide on a steam bath for one hour. The catalyst was filtered and washed repeatedly with water. The filtrate was acidified and chlorine ion was titrated potentiometrically with silver nitrate. Assuming hydrolysable chlorine to be silicon tetrachloride, the swept catalyst actually used in the reaction contained 1·60 g of silicon tetrachloride supported on 49·96 g of alumina.

When the temperature of the catalyst was brought to 400°C the flow of silicon tetrachloride and formaldehyde was begun. Metered dry nitrogen was used as an inert carrier for both reactants. Silicon tetrachloride was volatilized from a bubbler, and its vapour was mixed with formaldehyde just prior to entering the reaction zone (Fig. 1). Over a period of 4·5 hr 5·13 g of silicon tetrachloride and 3·4 g of formaldehyde were allowed to react. The time of contact with the catalyst was approximately 32 sec. The products which were condensable at −196°C were removed from the exit gases in a series of four U-traps immersed in liquid nitrogen. After completion of the reaction, the catalyst was swept at 400°C for 2 hr with dry nitrogen.

The volatile products were fractionated in a vacuum apparatus. They included 1010 cm^3* of hydrogen chloride, 55 cm^3 of carbon dioxide,† 905 cm^3 of methyl chloride (mol. wt. found 50·7, calc. 50·5), 30·8 cm^3 of methylene chloride (mol. wt. found 86, calc. 85), and 1·495 g of silicon tetrachloride (mol. wt. found 170, calc. 170; vapour tensions at 0·0°C, 10·0°C, and 20·0°C found 77·1, 124·1 and 191 mm respectively, reported[6] 77, 124, and 191 mm). No non-condensable gas was formed when the products were treated with aqueous alkali.

The reaction tube and catalyst were cooled in a stream of nitrogen and re-weighed, and the

* Wherever mentioned, cm^3 refers to volume at standard temperature and pressure.

† The mixture of hydrogen chloride and carbon dioxide was resolved by dissolving it in aqueous alkali and titrating chloride ion potentiometrically with silver nitrate after the solution was acidified.

[4] L. J. BELLAMY *The Infra-red Spectra of Complex Molecules* p. 280. John Wiley, New York (1954).
[5] A. W. SCHNITZER, G. J. FISHER, and A. F. MACLEAN *J. Amer. chem. Soc.* **75**, 4347 (1953).
[6] K. KEARBY *J. Amer. chem. Soc.* **58**, 374 (1936).

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catalyst (52·84 g) was removed and treated with 300 ml of a 0·27 M solution of sodium hydroxide on a steam bath for 1 hr. The catalyst was filtered and washed repeatedly with water. The filtrate was acidified (whereupon silica precipitated and was identified) and chloride ion was titrated potentiometrically with silver nitrate. Assuming hydrolysable chloride to be silicon tetrachloride, the used catalyst contained 1·71 g of silicon tetrachloride. The washed catalyst was brought to constant weight at 400°C in a stream of nitrogen. It then was swept with oxygen at 400°C until its colour approached chalk white, cooled, and re-weighed. The amount of carbon removed was 0·07 g.

The weights of silicon tetrachloride and carbon on the used catalyst accounted for only 1·78 of the 2·88 g of material which the used catalyst contained in addition to alumina. When the remaining 1·10 g of material on the used catalyst was considered to be silica, 94 per cent of the silicon entering the reaction as silicon tetrachloride could be accounted for in the volatile and non-volatile products. The assumption that the siliceous material on the catalyst consisted of 1·71 g of silicon tetrachloride and 1·10 g of silica was an arbitrary matter of convenience. The product may have consisted of

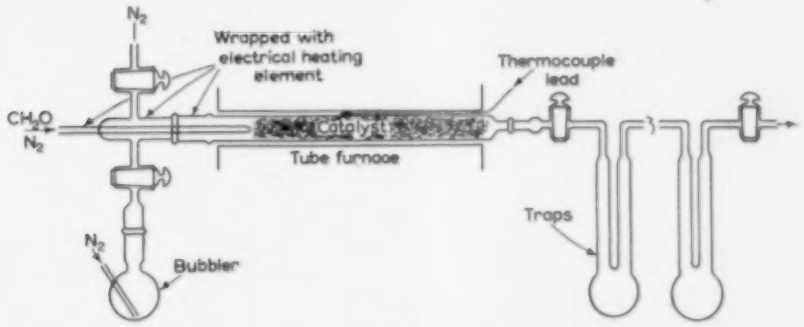

FIG. 1.

silica and silicon tetrachloride, or of chlorosiloxanes, or of all three. However, since any chlorosiloxane or mixture of chlorosiloxanes could be considered for the purposes of analysis to be a mixture of silica and silicon tetrachloride, it was convenient to consider the non-volatile product in this case in the same way without specifying its exact identity.

In all, 6·73 g (39·6 millimole) of silicon tetrachloride was introduced into the reaction. There was recovered from the reaction 18·8 millimoles of silicon tetrachloride, 18·3 millimoles of silica, 45·1 millimoles of hydrogen chloride, 40·4 millimoles of methyl chloride, and 1·4 millimoles of methylene chloride. The recovered materials accounted for 94 per cent of the silicon and 103 per cent of the chlorine which were introduced into the reaction as silicon tetrachloride.

Decomposition of chloromethoxytrichlorosilane over alumina. Alumina which was prepared by igniting Aluminum Company of America F-1 activated alumina (1/4 inch) at 650°C for 4 hr was poured directly into a Pyrex tube with an inside diameter of 20 mm, and it was swept first at 400°C with silicon tetrachloride in a stream of nitrogen and then at 200°C with nitrogen for 12 hr. Chloromethoxytrichlorosilane was carried over the alumina at 200°C in a stream of metered dry nitrogen, and the products were condensed in a series of four U-traps at −196°. In a typical reaction, 2·222 g of chloromethoxytrichlorosilane were passed over the alumina in 8·5 hr with the time of contact with the catalyst being 52 sec. There were obtained from the reaction 62 cm³ of hydrogen chloride (mol. wt. found 3·66, calc. 36·5), 74 cm³ of methyl chloride (mol. wt. found 50·7, calc. 50·5), 73 cm³ of methylene chloride (mol. wt. found 86, calc. 85), 0·840 g of silicon tetrachloride, 0·064 g of hexachlorodisiloxane (mol. wt. found 310 ± 3, calc. 285), and a gain in the weight of the catalyst of 0·686 g which was considered to be polymeric (Cl_2SiO) as before. In four such reactions, an average of 11·90 millimoles of chloromethoxytrichlorosilane gave 3·86 millimoles of hydrogen chloride, 3·49 millimoles of methyl chloride, 3·44 millimoles of methylene chloride, 5·02 millimoles of silicon tetrachloride, 0·23 millimole of hexachlorodisiloxane, and 6·51 millimoles of (Cl_2SiO), with average recovery of silicon and chlorine from the chloromethoxytrichlorosilane being 101 and 102 per cent respectively.

DISCUSSION

Passage of a mixture of silicon tetrachloride and formaldehyde over activated alumina at 400°C gave principally hydrogen chloride, methyl chloride, and chlorosiloxanes or silica, plus small amounts of methylene chloride:

$$SiCl_4 + 2CH_2O \longrightarrow SiO_2 + 2CH_2Cl_2$$

$$SiCl_4 + 4CH_2O \longrightarrow SiO_2 + 2CH_3Cl + 2HCl + 2CO$$

In some experiments small amounts of bis(chloromethyl) ether also appeared among the products of the reaction. All reactions were accompanied by deposition of carbon on the catalyst. The absence of mono-, di-, and tri-chlorosilane in the volatile products was demonstrated by the lack of their characteristic infra-red absorption bands and by the absence of hydrogen upon alkaline hydrolysis. That methyl chloride was formed to such an extent here and was not detected by GLEMSER and LOHMANN,[3] and that mono- and di-chlorosilane which they claim to be products of the reaction were not found here even in trace amounts, lead us to suggest that perhaps in their identification of the products by measurements of their vapour tensions methyl chloride and methylene chloride were mistakenly identified as mono- and di-chlorosilane.

The conversion of silicon tetrachloride to chlorosiloxanes or silica by its reaction with formaldehyde over alumina at 400°C might be attributed to actual hydrolysis of silicon tetrachloride by water arising from the decomposition of formaldehyde. We found water among the decomposition products of formaldehyde which was allowed to decompose under similar conditions over alumina, but the amount of water formed was far less than that which would be required to account for the reaction here. Furthermore, the amount of carbon which was deposited on the catalyst during the reaction of silicon tetrachloride with formaldehyde was much less than that which would be anticipated if formaldehyde were decomposing to carbon and water to an extent which would account for the entire reaction.

Water for the hydrolysis of silicon tetrachloride might, however, have arisen from the reaction of formaldehyde with hydrogen chloride:

$$2CH_2O + 2HCl \longrightarrow ClCH_2OCH_2Cl + H_2O$$

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

Indeed, in some experiments bis(chloromethyl) ether was found among the products of the reaction. Pyrolysis of the bis(chloromethyl) ether over alumina might account for some of the formation of methyl chloride and methylene chloride:

$$ClCH_2OSiCl_3 \longrightarrow CH_2Cl_2 + CH_2O$$

$$ClCH_2OSiCl_3 \longrightarrow CH_3Cl + HCl + CO$$

Finally, the reaction of silicon tetrachloride with formaldehyde over alumina might have occurred by a direct reaction of the two. Chloromethoxytrichlorosilane, $ClCH_2OSiCl_3$, has been obtained as a product of the uncatalysed vapour-phase reaction of silicon tetrachloride with formaldehyde:[7]

$$SiCl_4 + CH_2O \longrightarrow ClCH_2OSiCl_3$$

[7] R. E. FROST and E. G. ROCHOW *J. inorg. nucl. Chem.* **5**, 201 (1957).

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When pure chloromethoxytrichlorosilane (prepared independently by the chlorination of methoxytrichlorosilane)[8] was passed over alumina which had been treated previously with silicon tetrachloride, approximately equivalent amounts of hydrogen chloride, methyl chloride, and methylene chloride, plus silicon tetrachloride and a gain in the weight of the catalyst, were obtained. When the gain in the weight of the catalyst was considered again to be a polymer of (Cl_2SiO), 101 per cent of the silicon and 102 per cent of the chlorine entering reaction as chloromethoxytrichlorosilane could be accounted for in the volatile and non-volatile products. That the product of the reaction of silicon tetrachloride with formaldehyde over alumina at 400°C contained only a small amount of methylene chloride might be explained by the reduction of methylene chloride to hydrogen chloride and methyl chloride at the elevated temperature by hydrogen from the decomposition of formaldehyde. We have tested this hypothesis and have obtained methyl chloride by reaction of methylene chloride with hydrogen over alumina at 400°C.

The formation of methylene chloride and of polymeric (Cl_2SiO) by the reaction of chloromethoxytrichlorosilane over alumina at 200°C

$$ClCH_2OSiCl_3 \xrightarrow{\text{alumina}} CH_2Cl_2 + (Cl_2SiO)$$

is similar to the reaction of chloromethoxytrichlorosilane with aluminium chloride,[7]

$$ClCH_2OSiCl_3 + AlCl_3 \longrightarrow CH_2Cl_2 + Cl_2AlOSiCl_3$$

and might occur either by reaction of chloromethoxytrichlorosilane with aluminum–chlorine bonds on the surface of the alumina, if they be formed when activated alumina is treated with silicon tetrachloride, or by reaction of chloromethoxytrichlorosilane with silicon–chlorine bonds which may be activated by adsorption of silicon tetrachloride on the surface of activated alumina. The presence of silicon tetrachloride in the product of the reaction indicated that in addition to formation of methylene chloride and (Cl_2SiO), chloromethoxytrichlorosilane decomposed to silicon tetrachloride and formaldehyde, and detection (by infra-red spectrum) of carbon monoxide in the gaseous product indicated that formaldehyde decomposed further to carbon monoxide and hydrogen:

$$ClCH_2OSiCl_3 \longrightarrow SiCl_4 + CH_2O$$

$$CH_2O \longrightarrow H_2 + CO$$

Methyl chloride and hydrogen chloride may have been formed by reduction of methylene chloride by hydrogen from the decomposition of formaldehyde, or it may have arisen from reaction of formaldehyde with the silicon tetrachloride-swept alumina or with hydrogen chloride.

We conclude that the reaction of silicon tetrachloride with formaldehyde over our alumina catalyst at 400°C resulted in the formation of hydrogen chloride plus methylene and methyl chlorides, and in the deposition of a polymeric chlorosiloxane on the catalyst. We believe that the most probable route for this reaction is through the intermediate formation of chloromethoxytrichlorosilane, since this has been shown independently to result from the combination of the present reactants and since its

[8] Robert E. Frost Thesis, Library of Harvard University (1957).

decomposition over alumina has been shown to produce in approximately the same ratio all of the reaction products here observed.

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RADIATION-INDUCED NITRITE FORMATION FROM CONCENTRATED NITRATE SOLUTIONS

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Abstract—The γ-radiation-induced decomposition of nitrate solutions to form nitrite was investigated in the concentration range 0·001–5·0 M for a variety of nitrate salts. The nitrite formed was detected by the reduction of cerium(IV) ions present in solution during the irradiation. The enhanced cerium(III) yields were interpreted to be due to the formation of nitrite by direct action. The nitrite yield was found to be (1) independent of cation, (2) dependent upon the nitrate concentration, (3) dependent upon the total energy absorbed by the solution and (4) representable by the equation $G(NO_2^-)_{-da} = 1{\cdot}22 \log [NO_3^-] + 1{\cdot}70$, where $G(NO_2^-)_{-da}$ is the direct action formation of nitrite and $[NO_3^-]$ is the nitrate molarity.

IN 1907 THIELE[1] reported that nitrite was formed when a solution of potassium nitrate was exposed to the emissions of a quartz–mercury arc lamp. Since that time many investigators have irradiated nitrate solutions using light,[1–13] X-rays,[14–16] γ-rays,[17, 18] and fission fragments.[17] Most of them agree that nitrite and oxygen are produced from the decomposition of nitrate and some have reported that the decomposition proceeds more rapidly in basic than in acid solution. Most of the previous work on the decomposition of aqueous nitrate solutions has been performed on dilute solutions. The purpose of this research was to investigate the cobalt-60 γ-ray decomposition of concentrated metal nitrate solutions. Of particular interest were the parameters: nitrate concentration, associated cation, and physical properties of the salt.

When concentrated nitrate solutions are irradiated high yields of nitrite are observed. These yields cannot be explained satisfactorily by the currently accepted radical yields in water, therefore, an additional process must be contributing to the production of nitrite. SWORSKI[18] has demonstrated that these increased yields of

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[12] D. BERTHELOT and H. GAUDECHON *Ibid.* **152**, 522 (1911).
[13] E. WARBURG *S.B. preuss. Acad. math.-phys. Kl.* 1228 (1918); *Chem. Abstr.* **14**, 1930 (1920).
[14] W. T. ANDERSON, JR. *J. Amer. chem. Soc.* **46**, 797 (1924).
[15] G. L. CLARK and L. W. PICKETT *Ibid.* **52**, 465 (1930).
[16] C. MONTEMARTINI and E. VERNAZZA *Industr. Chim.* **7**, 588 (1932); *Chem. Abstr.* **26**, 5025 (1932).
[17] J. W. BOYLE and H. A. MAHLMAN Paper presented Amer. Nuc. Soc. Second Annual Meeting, Chicago Illinois (1956).
[18] T. J. SWORSKI *J. Amer. chem. Soc.* **77**, 4689 (1955).

nitrite are not the result of radical reaction and has used the term "direct action" to describe the enhancement. He has suggested several methods whereby increased yields of nitrite might arise.

It was thought that nitrite could be formed by two types of reactions. In dilute solutions of nitrate the hydrogen atoms formed by the radiolysis of water may attack the nitrate ion[19] and as equations (1) and (2) show,

$$NO_3^- + H \rightarrow NO_2 + OH^- \quad (1)$$

$$2NO_2 + H_2O \rightarrow 2H^+ + NO_3^- + NO_2^- \quad (2)$$

every two hydrogen atoms that participate in this series of reactions produce one nitrite. As the concentration of the nitrate ion increases more hydrogen atoms react by reaction (1) instead of contributing to nitrite-destroying reactions.[20] Thus one realizes that the initial rate of nitrite production by this process reaches a limit at the nitrate concentration where all hydrogen atoms react by this route. It is recognized that the nitrite yield may be increased by the nitrate ion reacting with some of the hydrogen atoms that normally interact with each other to form molecular hydrogen. If the nitrite concentration is increased by this process it is limited to the molecular hydrogen production and would probably be dependent upon some function of the nitrate ion concentration. Also as the nitrate concentration increases, the probability of direct interaction of the radiation with the nitrate ion increases. This may occur by interaction of the incident γ-ray, the scattered γ-ray, the ejected electron or by energy transfer from excited water molecules with the nitrate ion. Since the purpose of this research is to determine the amount of enhanced nitrite yield, no distinction will be made with respect to its mode of origination. The net reaction, as proposed for photolysis and X-ray irradiation of aqueous nitrate solutions may be represented as follows:[13,15]

$$NO_3^- \rightsquigarrow NO_2^- + \tfrac{1}{2}O_2 \quad (3)$$

but this representation is not meant to indicate the mechanism of γ-ray-induced nitrite formation.

The system utilized in this research was 0·4 M H_2SO_4 containing 0·0002 mole of cerium(IV) ions and the desired molarity of the nitrate salt. In the absence of added nitrates the rate of cerium(IV) reduction was observed to be 2·40 molecules per 100 eV of absorbed energy. This is in excellent agreement with the value 2·39 recently reported by SWORSKI.[21] Considering the reactions (1) and (2) in respect to the mechanism of cerium(IV) reduction in 0·4 M sulphuric acid solution, one would predict that in dilute nitrate solutions, where reaction (3) is negligible, the yield of cerium(III) would be the same as without nitrate. This was observed within the experimental error of our experiments.

In acid solution nitrite reduces cerium(IV) ions as follows:

$$NO_2^- + 2Ce^{IV} + H_2O \rightarrow 2Ce^{III} + 2H^+ + NO_3^- \quad (4)$$

Therefore in concentrated solutions where reaction (3) cannot be neglected, any increase in the cerium(III) yield may be assigned to the direct action process. Thus,

[19] N. A. BAKH *Conf. of the Acad. of Sci. of the U.S.S.R. on Peaceful Uses of Atomic Energy* (1955).
[20] H. A. SCHWARZ and A. O. ALLEN *J. Amer. chem. Soc.* **77**, 1324 (1955).
[21] T. J. SWORSKI *Rad. Res.* **4**, 483 (1956).

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measurements of the cerium(III) yield in acid solution containing cerium(IV) ions plus nitrate should provide the data necessary to calculate the nitrite produced by direct action. In the system employed it was impossible to ascertain whether nitrite *per se* was formed and immediately reduced cerium(IV) ions or if an intermediate reduced the cerium(IV) ions. Perhaps the term nitrite equivalent would be suitable, but since nitrite is the major product in the absence of cerium(IV) ions, the data are expressed in terms of nitrite formation. Assuming that the nitrite ion is the reacting entity in an acid solution of cerium(IV) ions[22] the yield of nitrite by direct action will be equal to one-half of the enhanced cerium(III) yield.

APPARATUS AND MATERIALS

The γ-radiation employed in the investigation was obtained from a cobalt-60 γ-ray source consisting of about 150 c.[23] The spectrophotometric measurements were made on a Cary Model 11 MS Recording Spectrophotometer. The irradiation cells, supplied by Pyrocell Manufacturing Company, New York, had special fused quartz windows that were not coloured by γ-radiation. Thus the irradiations and spectrophotometric determinations were made using the same cells. All water used was distilled from a Barnstead still, then re-distilled from an acid permanganate solution, then from a basic permanganate solution and then in an all silica system. The water was stored in silica containers. All chemicals used were reagent grade.

EXPERIMENTAL

Determinations of iron(III) were made directly at 3050 Å where the molar extinction coefficient has been found to be 2240 at 25°C.[24] Determination of the absorption of the cerium(IV) at 3300 Å[9] allowed the concentration of cerium(III) to be calculated by difference. The molar extinction coefficient of the cerium(IV) in 0·4 M sulphuric acid at 3300 Å was found to be 5359. Thorium interferes with the direct spectrophotometric determination of cerium(IV) in 0·4 M sulphuric acid. In these solutions the cerium(IV) was reacted with iron(II) and the resulting iron(III) determined colorimetrically by the thiocyanate method.[25]

The cobalt-60 γ-ray source was calibrated with the iron(II) dosimeter. The rate of energy absorption was calculated from the spectrophotometrically determined rate of iron(II) oxidation in the same irradiation cell. The rate of iron(II) oxidation in a 0·4 M H_2SO_4 solution as determined by a calorimetric calibration has been shown to be 15·6 $\pm$ 0·3 molecules of iron(II) oxidized per 100 eV of energy absorbed by the solution.[24]

A number of nitrate solutions of differing molarities and various cations were prepared. In addition to the nitrate salt the solutions were 0·0002 M in cerium(IV) and 0·4 M in sulphuric acid. These solutions were irradiated for varying times and the cerium(III) yields were determined on the basis of total energy absorbed by the solution. The amount of cerium(IV) reduction attributable to the radiolysis of the solvent (0·4 M sulphuric acid) based upon the total absorbed energy, was subtracted. The corrected cerium(III) yield represented the equivalent reduction by the direct-action process on the nitrate ion. With reference to reaction (4) the yield of nitrite was calculated. The experimentally determined direct-action nitrite yields for the nitrates of the alkali metals, ammonium, zinc, magnesium, aluminium and thorium are presented in Table 1.

DISCUSSION

The calculation of yield involved the determination of (1) the amount of energy absorbed and (2) the amount of product produced. The cerium(III) was determined by difference from the quantitative determinations of cerium(IV) as previously discussed. Since the aqueous portion of the dosimeter and the solvent are the same,

[22] W. W. Scott *Standard Methods of Chemical Analysis* Vol. 1. p. 1205, D. Van Nostrand, New York (1939).
[23] J. A. Ghormley and C. J. Hochanadel *Rev. sci. Instrum.* **22**, 473 (1951).
[24] C. J. Hochanadel and J. A. Ghormley *J. chem. Phys.* **21**, 880 (1953).
[25] F. D. Snell and C. T. Snell *Colorimetric Methods of Analysis* p. 310. D. Van Nostrand, New York (1949).

the energy absorbed per g of solvent was assumed to be the same as that absorbed in 1 g of dosimeter solution and was calculated by dividing the energy absorbed per ml of dosimeter solution by its density. It was assumed that the absorption of energy per g by the solvent and the solute was proportional to their respective γ-ray mass absorption coefficients. This coefficient, $g(T)$, is actually the sum of three individual

TABLE 1.—DIRECT ACTION NITRITE YIELDS

NO_3^- Molarity	Li	Na	K	Rb	Cs	NH_4	Zn	Mg	Al	Th
0·1	0·54	0·50	—	0·48	0·52	0·55	0·49	0·53	—	0·50
0·14	—	—	0·68	—	—	—	—	—	—	—
0·15	—	—	—	—	—	—	—	—	0·69	—
0·20	0·82	0·88	—	—	—	0·83	0·86	0·78	—	0·78
0·30	1·07	1·02	—	0·89	1·14	1·04	—	—	0·90	1·19
0·34	—	—	1·12	—	—	—	—	—	—	—
0·40	—	—	—	1·22	—	—	1·17	1·19	—	—
0·50	1·36	1·33	1·39	1·37	1·38	1·37	—	—	—	1·38
0·60	—	—	—	—	—	—	1·27	1·27	1·21	—
0·90	—	—	—	—	—	—	—	—	1·39	—
1·0	1·83	1·62	1·73	—	1·76	1·72	1·63	1·54	—	1·74
1·36	—	—	1·94	—	—	—	—	—	—	—
1·50	—	—	—	—	—	—	—	—	1·75	—
1·75	—	—	2·02	—	—	—	—	—	—	—
2·00	2·10	—	—	—	—	2·11	—	1·79	—	2·19
3·00	—	2·24	—	—	—	2·53	—	—	2·03	2·54
4·00	—	—	—	—	—	—	—	2·42	—	—
5·00	—	2·59	—	—	—	2·71	—	—	—	—

mass absorption coefficients which describe the efficiencies of the three major processes by which γ-rays lose energy.[26] These processes are known as the photoelectric effect, Compton scattering, and pair production, and their respective mass absorption coefficients will be symbolized by $g(P)$, $g(C)$, and $g(PP)$. Thus one may write:

$$g(T) = g(P) + g(C) + g(PP) \tag{5}$$

The individual mass absorption coefficients may be calculated for various atoms by using the following empirical equations:[27,28,29]

$$g(P) = aW^3 - bW^4 \tag{6}$$

$$g(C) = cA/Z \tag{7}$$

$$g(PP) = dZ\,(Z + 1)\,(E - 1{\cdot}02)/AE \tag{8}$$

where a, b, c, and d are constants, W is the wavelength of the incident γ-ray in ångströms, A is the atomic weight, Z is the atomic number, and E is the energy of the incident γ-ray in MeV. The values of $g(P)$ and $g(PP)$ for cobalt-60 γ-rays turn out

[26] D. HALLIDAY *Introductory Nuclear Physics* p. 139. John Wiley, New York (1950).
[27] J. A. VICTOREEN *J. appl. Phys.* **14**, 95 (1943).
[28] A. H. COMPTON and S. K. ALLISON *X-Rays in Theory and Experiment* p. 260. D. Van Nostrand, New York (1935).
[29] W. HEITLER *The Quantum Theory of Radiation* p. 200. Clarendon Press, Oxford (1936).

to be very small as compared to that of $g(C)$ except where Z is large. Using the relations given above, the $g(T)$ values were calculated for the various atoms involved in the study. The energy absorbed by the solute was that calculated using the values of $g(T)$ presented in Table 2. For example, the energy absorbed by the cation was calculated by use of the following equation:

$$E_{(C)} = \frac{E_{(gs)} \times g(T_c) \times W_{(C)}}{g(T_s)} \tag{9}$$

where $g(T_c)$ is the γ-ray mass absorption coefficient for the cation, $g(T_s)$ is the γ-ray mass absorption coefficient for the solvent, $W_{(C)}$ is the number of grammes of cation

TABLE 2.—CALCULATED γ-RAY MASS ABSORPTION COEFFICIENTS (cm^2/g)

Atom	$g(P)$	$g(C)$	$g(PP)$	$g(T)$
H	0·00000	0·05288	0·00000	0·05288
Li	0·00000	0·02304	0·00000	0·02304
N	0·00000	0·02663	0·00001	0·02664
O	0·00000	0·02665	0·00001	0·02666
Na	0·00000	0·02549	0·00002	0·02551
Mg	0·00001	0·02630	0·00002	0·02633
Al	0·00002	0·02569	0·00002	0·02572
S	0·00003	0·02660	0·00003	0·02666
K	0·00004	0·02590	0·00003	0·02597
Zn	0·00019	0·02445	0·00004	0·02468
Rb	0·00034	0·02308	0·00005	0·02347
Cs	0·00117	0·02207	0·00007	0·02331
Th	0·00550	0·02066	0·00011	0·02627

per ml of solution and $E_{(gs)}$ is the energy absorbed by 1 g of the solvent. The energy absorbed by the anion was calculated in a like manner. The total energy absorbed, expressed as eV/ml min, was obtained by summing the energies absorbed in the solvent, the cation and the anion, that is:

$$E = E_{(s)} + E_{(c)} + E_{(a)} \tag{10}$$

This value of E was then used to calculate G values for cerium(III) in the various experiments. The direct action yield of nitrite (Table 1) as determined by a least squares analysis of all the data may be represented by:

$$G(NO_2^-)_{-da} = 1{\cdot}22 \log [NO_3^-] + 1{\cdot}70 \tag{11}$$

where $G(NO_2^-)_{-da}$ represents the direct action nitrite yield and $[NO_3^-]$ represents the molar concentration of the nitrate ion. The slope (1·22) and the intercept (1·70) of equation (11) have standard errors of $\pm$0·02 and $\pm$0·01, respectively. This equation indicates that direct action practically ceases below a nitrate concentration of 0·04 M, since this is the point at which $G(NO_2^-)_{-da}$ becomes zero.

The consistency of this method of calculation, as evidenced in the experimental data, indicated that the energy absorbed by the constituent parts of the solution is

probably effective in decomposing nitrate to nitrite. There appeared to be no direct correlation between the physical properties of the nitrate salt or the cation and the rate of nitrite formation. The only variable determining the rate of nitrite formation appeared to be the nitrate concentration.

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COMPLEX FORMATION IN CUPRIC PHTHALATE SOLUTIONS

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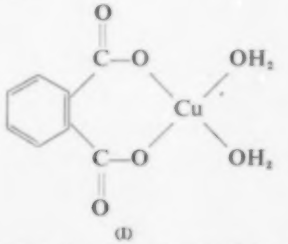
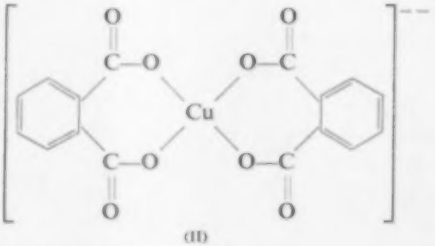
Abstract—Aqueous solutions of cupric phthalate have been studied spectrophotometrically. From the absorptions of the solutions at various ionic strengths with cupric ions in excess the first complexing constant ($K_1 = 2{\cdot}9 \times 10^2$) has been found and mean activity coefficients estimated at ionic strengths of 0·03 to 0·25. With phthalate ions in excess the second complexing constant ($K_2 = 23{\cdot}6$) has been determined.

ADDITION of the salts of carboxylic acids to cupric sulphate solutions alters the characteristic blue colour, the absorption band in the red region of the visible spectrum shifting to shorter wavelengths with increased extinction. The change in colour may be attributed to the formation of various cupric carboxylate complexes, depending on the stability of these complexes in solution. Thus the deep colour of solutions of cupric oxalate in alkali oxalates must be due to the cupri-oxalate ion, $Cu(C_2O_4)_2^{--}$, as the neutral salt is not soluble. Cupric malonate is soluble but the large values observed for the complexing constants[1,2,3] indicate that cupri-malonate ions, $Cu(CH_2C_2O_4)_2^{--}$, should be almost completely formed in solutions containing a cupric : malonate ion ratio of 1 : 2. The stability of this complex and also of the cupri-oxalate complex has been confirmed in this department spectrophotometrically, the absorption of solutions of cupric sulphate in alkali malonate or oxalate changing no further when the ratio of dicarboxylate to cupric ions exceeds about 2·5 : 1.

Cupric phthalate, like the malonate, is soluble in water giving a deeply coloured solution. Addition of alkali phthalate to this solution causes further intensification and a shift of the absorption band to shorter wavelength, but in this case further addition of alkali phthalate continues to affect the absorption even when the alkali phthalate is already present in large excess (Table 4). Molecular cupric phthalate (I) and the complex cupri-phthalate ion (II) are thus much less stable than the corresponding oxalate and malonate complexes and probably less stable even than the carbonate complex, $Cu(CO_3)_2^{--}$, which is formed in very strong alkali carbonate solutions.



(I)



(II)

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[1] D. J. G. IVES and H. L. RILEY *J. chem. Soc.* 1998 (1931).
[2] J. M. PEACOCK and J. C. JAMES *J. chem. Soc.* 2233 (1951).
[3] E. GELLES and G. H. NANCOLLAS *J. chem. Soc.* 4847 (1956).

This instability is no doubt due to the resistance offered by the formation of the seven membered ring.

Table 1 shows the effect of dilution on solutions with various cupric ion : phthalate ion ratios. From the table it is apparent that whereas the absorption is affected by dilution in the presence of excess phthalate, when cupric ion is in excess the absorption is almost independent of dilution. This indicates a considerable difference in the equilibrium constants of the two steps in cupri-phthalate ion formation, the formation

TABLE 1.—DILUTION OF CUPRIC PHTHALATE SOLUTIONS

$\frac{[Cu^{++}]}{[C_6H_4C_2O_4^{--}]}$	$CuSO_4$ (moles/l.)	$C_6H_4(CO_2Na)_2$ (moles/l.)	ε	λ (mμ)
$\frac{4}{1}$	0·02	0·005	16·9	770
	0·04	0·01	17·0	770
	0·08	0·02	17·0	770
$\frac{2}{1}$	0·01	0·005	22·4	750
	0·02	0·01	22·8	753
	0·04	0·02	23·1	750
$\frac{1}{1}$	0·01	0·01	31·0	740
	0·02	0·02	32·7	740
	0·04	0·04	33·3	735
$\frac{1}{2}$	0·005	0·01	38·9	730
	0·01	0·02	42·1	725
	0·02	0·04	45·0	720
$\frac{1}{4}$	0·005	0·02	46·8	715
	0·01	0·09	50·7	710
	0·02	0·08	56·0	707

of molecular cupric phthalate being almost complete even with equivalent concentrations of cupric and phthalate ions. It is thus permissible to use the extinction (or the wavelength, in this case a less sensitive characteristic) of the absorption band as a measure of the state of equilibrium of the first step in complex formation when cupric ions are in excess and of the second step when phthalate ions are in excess; provided that appropriate extinctions can be assigned to the three species hydrated cupric ion (ε_0), molecular cupric phthalate (ε_1) and cupri-phthalate ion (ε_2).

An accurate value for ε_0 can be obtained in cupric sulphate solutions. Approximate values of ε_1 and ε_2 can be estimated from Table 4 (ε_1 = ca. 35, ε_2 = ca. 75). The actual values of ε_0, ε_1 and ε_2 used in the determination of the equilibrium constants were obtained by trial and error so as to give the most reproducible values of the equilibrium constants assuming a linear relationship between the extinction and the proportions of each absorbing species present. The value of ε_0 obtained in this way (10·8) is a little lower than that observed in cupric sulphate solutions (11·6).

As the first step in the equilibrium may be expected to respond considerably to changes in ionic strength, the equilibrium constant for this step was determined at

several different ionic strengths, controlled by the addition of suitable amounts of sodium sulphate. Table 2 shows the calculation of these equilibrium constants.

The mean values of the concentration constants (k_1) derived from Table 2 may

TABLE 2.—CALCULATION OF THE FIRST COMPLEXING CONSTANT AT VARIOUS IONIC STRENGTHS

$\varepsilon_0 = 10{\cdot}8 \qquad \varepsilon_1 = 36{\cdot}5$

μ	$CuSO_4$ (mole/l.)	Na_2Ph (mole/l.)	ε	% Cu as CuPh	Conc. at equilibrium			$k_1 \times 10^{-3}$
					CuPh	Cu aq^{++}	Ph^{--}	
	0·005	0·005	29·4	72·4	0·00362	0·00138	0.00138	1·91
0·03	0·008	0·004	22·2	44·4	0·00355	0·00445	0·00045	1·77
	0·005	0·005	28·6	69·2	0·00346	0·00154	0·00154	1·46
0·06	0·01	0·01	30·6	77·0	0·00770	0·00230	0·00230	1·46
	0·01	0·005	22·1	44·0	0·00440	0·00560	0·00060	1·32
	0·005	0·005	27·6	65·4	0·00327	0·00173	0·00173	1·09
	0·01	0·01	29·5	72·7	0·00727	0·00273	0·00273	0·98
0·12	0·02	0·02	31·6	80·9	0·01618	0·00382	0·00382	1·12
	0·01	0·005	21·8	42·8	0·00428	0·00572	0·00072	1·08
	0·02	0·01	22·3	44·7	0·00894	0·01106	0·00106	0·76
	0·02	0·005	16·9	23·7	0·00474	0·01526	0·00026	1·19
	0·005	0·005	26·0	59·1	0·00296	0·00204	0·00204	0·71
	0·01	0·01	28·3	68·1	0·00681	0·00319	0·00319	0·67
	0·02	0·02	30·3	75·9	0·01518	0·00482	0·00482	0·72
	0·04	0·04	32·5	84·4	0·03376	0·00624	0·00624	0·87
0·25	0·01	0·005	21·3	40·9	0·00409	0·00591	0·00091	0·76
	0·02	0·01	22·0	43·6	0·00872	0·01128	0·00128	0·60
	0·04	0·02	22·8	46·7	0·01868	0·02132	0·00132	0·67
	0·02	0·005	16·9	23·7	0·00474	0·01526	0·00026	1·19
	0·04	0·01	17·0	24·1	0·00964	0·03036	0·00036	0·97

be extrapolated to give the activity constant (K_1) for zero ionic strength by plotting $\log k_1$ against $\sqrt{\mu}$ according to the relationship:

$$\log k_1 = \log K_1 - A\sqrt{\mu}$$

where A is a proportionality constant dependent upon solvent, temperature and the valencies of the ions involved. The mean activity coefficient for ionized cupric phthalate at each ionic strength may then be derived from the equation:

$$k_1 = f_{\pm}^{2} K_1$$

assuming an activity coefficient of unity for molecular cupric phthalate. The results are shown in Table 3, together with activity coefficients calculated by Davies' approximation formula:[4]

$$-\log f_{\pm} = 0{\cdot}50 z_+ z_- \left\{ \frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0{\cdot}20\ \mu \right\}$$

[4] C. W. DAVIES *J. chem. Soc.* 2093 (1938).

The value of the activity constant, $K_1 = 2{\cdot}9 \times 10^3$, may be compared with that obtained potentiometrically ($K_1 = 1{\cdot}2 \times 10^4$) by PEACOCK and JAMES.[2] These authors do not state the ionic strength used in their determination but the activity coefficients were calculated by Davies' formula and so were probably too small by a factor of 1·6 to 1·8. Correction of their value of K_1 to take into account the abnormally high activity coefficient of ionized cupric phthalate gives a revised value of $K_1 = 4 \times 10^3$ in good agreement with the spectrophotometric value now obtained.

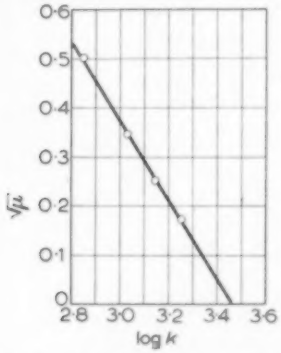

FIG. 1.—Graph showing extrapolation of the first equilibrium constant to zero ionic strength.

A possible source of error in our determination may arise from ion-pair formation between cupric and sulphate ions reducing the concentration of free cupric ions in the solution, though the equilibrium constant for this reaction[4] taken in conjunction with the low activity coefficients in cupric sulphate solutions indicates that only a small fraction of the cupric ions present in solution could be removed in this way.

TABLE 3.—ACTIVITY COEFFICIENTS OF IONIZED CUPRIC PHTHALATE

μ	0·25	0·12	0·06	0·03	0·0
Mean k_1 ($\times 10^{-3}$)	0·71	1·07	1·41	1·8	2·9
$f_\pm$	0·50	0·61	0·70	0·79	1
$f_\pm$ (DAVIES)	(0·27)	0·34	0·43	0·52	1

Experiments in which sodium perchlorate, nitrate or chloride was used instead of the sulphate to control the ionic strength gave extinctions almost identical with those observed using sodium sulphate (within 5 per cent even at high ionic strengths and nearer at lower ionic strengths when the difference of 1–3 per cent is of the order of experimental error).

It thus appears that any error in the extrapolated value of K due to this cause is likely to be small (less than 10 per cent) and sodium sulphate is preferred to the other salts for controlling ionic strength on account of the greater experimental accuracy obtainable, the stoichiometrically simple relationship in the ion-pair formation and the fact that the reaction between cupric and sulphate ions has been previously studied.

Table 4 shows the calculation of the second complexing constant:

$$k_2 = \frac{[Cu(C_6H_4C_2O_4)_2^{--}]}{[Cu(C_6H_4C_2O_4)(OH_2)_2] \times [C_6H_4C_2O_4^{--}]}$$

The absorption spectra with phthalate ions in excess are less sensitive to changes in ionic strength, the activity coefficients of the two anions probably being similar. On the assumption that the activity coefficient of molecular cupric phthalate is unity the mean value of the activity constant, $K_2 = 23{\cdot}6$, is obtained directly from the table

TABLE 4.—CALCULATION OF THE SECOND COMPLEXING CONSTANT

$\varepsilon_1 = 36{\cdot}5 \qquad \varepsilon_2 = 73{\cdot}5$

$CuSO_4$ (mole/l.)	Na_2Ph (mole/l.)	λ (mμ)	ε	% Cu as $CuPh_2^{--}$	Conc. at equilibrium			k_2
					$CuPh_2^{--}$	CuPh	Ph^{--}	
0·005	0·02	715	46·8	27·8	0·00139	0·00361	0·01361	28·3
0·005	0·05	708	56·7	54·6	0·00273	0·00227	0·04227	28·5
0·01	0·04	710	50·7	38·4	0·00384	0·00616	0·02616	23·8
0·01	0·10	700	60·8	65·7	0·00657	0·00343	0·08343	23·0
0·02	0·05	715	48·6	32·7	0·00654	0·01346	0·02346	20·7
0·02	0·08	707	56·0	52·7	0·01054	0·00946	0·04946	22·5
0·02	0·10	703	59·0	60·8	0·01216	0·00784	0·06784	22·9
0·02	0·20	698	65·4	78·0	0·01560	0·00440	0·16440	21·6
0·02	0·50	695	70·5	91·9	0·01838	0·00162	0·46162	24·6
0·04	0·08	715	48·2	31·6	0·01264	0·02736	0·02736	16·9
0·04	0·16	700	63·0	71·5	0·02860	0·01140	0·09140	27·2

The characteristic extinction of the absorption band of cupric phthalate is thus found to be $\varepsilon_1 = 36{\cdot}5$ ($\lambda = 735$ mμ) and of the cupri-phthalate ion $\varepsilon_2 = 73{\cdot}5$ ($\lambda = 690$ mμ). The values of the two complexing constants are found to be $K_1 = 2{\cdot}9 \times 10^3$ and $K_2 = 23{\cdot}6$.

EXPERIMENTAL

Cupric ions were introduced as standard solutions prepared from Analar cupric sulphate crystals; phthalate ions as standard solutions prepared from resublimed phthalic anhydride and the equivalent amount of anhydrous sodium carbonate.

Absorption spectra were determined on a Unicam SP500 spectrophotometer using glass cells of 1 cm path.

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 224 to 228. Pergamon Press Ltd., London

THE SYSTEM BORON TRIFLUORIDE–HEAVY WATER; HYDROXYTRIFLUOROBORIC ACID-d_2: D[BF_3·OD]

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(*Received* 24 *April* 1957)

Abstract—The 1:1 addition compound between boron trifluoride and heavy water has been prepared and its properties compared with those of the normal monohydrate in order to obtain more information on the nature of the conduction process in these liquids. The compound melts at 11·0° and at this temperature the density is 1·8360 g ml^{-1}, the viscosity 12·21 cP, and the specific conductivity $1{\cdot}835 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$.

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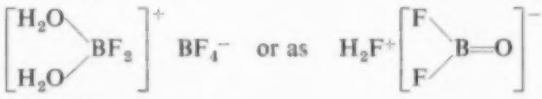
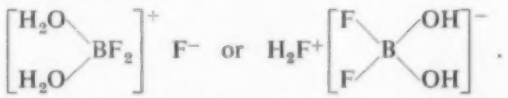
PREVIOUS work has shown that the hydrates of boron trifluoride are extensively dissociated into ions in the molten state.[1] Electrolysis experiments have been interpreted in terms of the ions $H^+[BF_3{\cdot}OH]^-$ for the monohydrate, the proton being solvated with an undissociated molecule of the complex BF_3,H_2O to give $[H_3O{\cdot}BF_3]^+[BF_3{\cdot}OH]^-$. This process is analogous to the autoprotolysis of sulphuric acid: $SO_3,H_2O \rightarrow H^+[SO_3{\cdot}OH]^- \rightarrow [H_3O{\cdot}SO_3]^+[SO_3{\cdot}OH]^-$, i.e. $[H_3SO_4]^+[HSO_4]^-$. The dihydrate was formulated as hydroxonium hydroxytrifluoroborate, $[H_3O]^+[BF_3{\cdot}OH]^-$. Alternative but less likely schemes have also been proposed. Thus the monohydrate could be regarded as



and the dihydrate could be written as



These formulations differ obviously in the relative proportions of the various atoms transported by the ions to the cathode and anode. In order (a) to confirm the ionic species proposed on the bases of the gaseous products of electrolysis, (b) to determine the transport number and mobility of the ions, and (c) to obtain more information about the conduction process in these liquids, isotope tracer experiments were undertaken. Either separated boron isotopes or radiofluorine would be feasible as tracers but deuterium was selected as being the most readily available and the simplest to handle.

As a preliminary to the transport measurements, it was necessary to know the properties of the pure compounds BF_3,D_2O and $BF_3,2D_2O$. These properties are reported in this and the following paper and are compared with those of the corresponding proton-hydrates. Certain information about the conduction process may be deduced from this comparison but the main tracer experiments will be reported in detail later.

[1] N. N. GREENWOOD and R. L. MARTIN *J. chem. Soc.* 1915 (1951).

EXPERIMENTAL

Boron trifluoride (supplied by Imperial Smelting Corporation) was absorbed in heavy water [99·95 per cent D_2O] until the latter was saturated at 0°. The complex so formed had the composition BF_3,1·0013D_2O; it melted at 9·9° and had a dissociation pressure of considerably more than 1 atm at room temperature. Purification by fractional freezing in a sealed, glass U-tube raised the m.p. to 11·0–11·1°, more than 5° above the m.p. of the monohydrate 5·9–6·0°. No temporary, flocculent, white precipitate was observed similar to that obtained in the system with water;[1]

TABLE 1.—DENSITY AND VISCOSITY OF D[BF_3·OD] BETWEEN 5 AND 20°

t°	d_4^t g ml^{-1}	ν cS	η cP	ϕ cP^{-1}
5·00	1·8430	7·77	14·33	0·0698
6·00	—	7·57	13·93	0·0718
7·00	1·8406	7·37	13·57	0·0737
8·00	—	7·18	13·20	0·0758
9·00	1·8392	7·01	12·88	0·0776
10·00	1·8370	6·84	12·57	0·0796
11·00	1·8360	6·65	12·21	0·0819
12·00	1·8348	6·19	11·91	0·0840
13·00	1·8337	6·31	11·57	0·0864
15·00	1·8313	6·01	11·01	0·0908
17·00	(1·8284)	5·72	10·47	0·0955
20·00	1·8255	5·32*	9·71*	0·1030*

* Calculated by extrapolation of the linear plot of log η against $1/T$°K.

this may reflect the tendency of deuterium compounds to react more slowly than their hydrogen analogues, the critical concentration range being passed before precipitation and redissolution could take place.

The electrical conductivity was measured at 1000 c/s,[2] and remained unchanged over a period of days. Viscosity was measured in a conventional U-tube apparatus in which the two limbs were joined to a stop-cock and to silica-gel guard tubes by short lengths of polythene tubing. To avoid contamination, the liquid level was not adjusted at each temperature but the height of the initial charge was noted and an appropriate correction applied. Because of the small temperature range investigated this correction was never more than 1 part in 400 of the measured viscosity. Density was measured in a Pyrex-glass dilatometer and was corrected for bouyancy and for thermal expansion of the glass.

RESULTS

The density of purified D[BF_3·OD] in the temperature range 5–20° is given in Table 1; the values correspond to the equation

$$d_4^t = 1{\cdot}8482 - 1{\cdot}11 \times 10^{-3}t.$$

It is interesting to observe that the density maximum in heavy water itself, which occurs at 11·2°, is not apparent in the 1:1 complex with boron trifluoride, the structure

[3] N. N. GREENWOOD and I. J. WORRALL *J. inorg. nucl. Chem.* **3**, 357 (1957).

of the heavy water having been entirely altered during complex formation. The density of $D[BF_3 \cdot OD]$ is some 2·2 per cent higher than that of $H[BF_3 \cdot OH]$ but, because of the greater molecular weight of the deuterium compound, the molar volume of the two complexes is very similar (see Table 3). In this the complexes parallel the behaviour of most deuterium compounds, the volume requirements of the hydrogen and deuterium atoms being almost identical.

The viscosity of the monodeuterate in the same temperature range is also presented in Table 1. Readings could not be obtained above 17° because of the evolution of gaseous boron trifluoride from the complex. A plot of log η against $1/T$°K is essentially linear throughout the temperature range studied and corresponds to an activation

TABLE 2.—ELECTRICAL CONDUCTIVITY OF MOLTEN $D[BF_3 \cdot OD]$ BETWEEN 0 AND 20°

t°	$10^3\kappa\ \Omega^{-1}\ cm^{-1}$	$\mu\ \Omega^{-1}\ cm^2$	$\mu\eta\ \Omega^{-1}\ cm^2\ cP$
0·00	1·392	0·6616	(10·87)
5·00	1·587	0·7565	10·84
7·00	1·666	0·7952	10·79
9·00	1·750	0·8363	10·77
10·00	1·792	0·8570	10·77
11·00	1·835	0·8780	10·72
12·00	1·879	0·8997	10·71
13·00	1·923	0·9212	10·66
15·00	2·013	0·9657	10·63
17·00	2·104	1·010	10·58
20·00	2·248	1·082	10·50

energy for viscous flow, E_η, of 4·21 kcal mole^{-1}. The viscosity of the complex with heavy water is very similar to that of the monohydrate; the two values are identical at about 17° but the monodeuterate has a somewhat larger temperature coefficient.

The electrical conductivity data are summarized in Table 2. These figures were obtained at 1000 c/s and were stable over a period of days. At 5000 c/s the readings were 0·3 per cent higher. The conductivity is $1{\cdot}835 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at the m.p. and increases to $2{\cdot}248 \times 10^{-2}$ at 20°. This latter figure corresponds to a molar conductivity, μ, of 1·082 $\Omega^{-1}\ cm^2$ and a reduced conductivity, $\mu\eta$, of 10·50 $\Omega^{-1}\ cm^2$ cP, a value which is almost constant throughout the temperature range studied. Reference to Table 3 indicates how close these values are to those of the monohydrate. A logarithmic plot of conductivity against the reciprocal of the absolute temperature shows a pronounced discontinuity at 12°; above this temperature the activation energy of conduction is 3·66 kcal mole^{-1} but in the supercooled region the activation energy is 6·3 per cent greater, i.e. 3·89 kcal mole^{-1}. It is curious that this discontinuity, which should reflect the influence of viscosity on ionic mobility,[3] is not found in the viscosity plot for this compound.

The decomposition potential of $D[BF_3 \cdot OD]$ was 2·5 V at 0°. Electrolysis resulted in the liberation of deuterium, oxygen, and boron trifluoride at the electrodes in the same way as for the monohydrate.[1] A back e.m.f. experiment gave a value of 1·6 V,

[3] N. N. GREENWOOD and R. L. MARTIN *Proc. roy. Soc.* A215, 46 (1952).

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a result which suggests an appreciable over-voltage under the conditions of measurement of the decomposition potential.

DISCUSSION

The properties of boron trifluoride monohydrate and monodeuterate at 20° are compared in Table 3. The most striking difference between the two compounds is in their m.p., the effect of substituting deuterium for hydrogen being to raise the value from 6·0° to 11·0°. This increase of 5·0° is greater than for any other isotopic pair of compounds yet reported except boron trifluoride dihydrate and dideuterate where the increase is 5·1°.[4] The density of the deuterium compound is

TABLE 3.—COMPARISON OF $H[BF_3{\cdot}OH]$ AND $D[BF_3{\cdot}OD]$ AT 20°

Property	$H[BF_3{\cdot}OH]$	$D[BF_3{\cdot}OD]$	ratio D/H
Mol. wt. g mole^{-1}	85·84	87·85	1·023
m.p. °C	5·9–6·0°	11·0–11·1°	1·018
d_4^{20} g ml^{-1}	1·7857	1·8255	1·022
V_M ml mole^{-1}	48·07	48·13	$1·001_2$
$V_M(BF_3)$ (apparent)	29·91	29·93	—
dd/dt g ml^{-1} deg^{-1}	$1·14 \times 10^{-3}$	$1·11 \times 10^{-3}$	0·974
ν cS	5·70	5·32	0·934
η cP	10·18	9·71	0·955
ϕ cP^{-1}	0·0982	0·1030	1·048
B cP ml g^{-1}	0·159	0·147	0·925
E_η kcal mole^{-1}	3·8	4·21	1·11
E_κ kcal mole^{-1}	3·6	3·66	1·02
$\kappa\ \Omega^{-1}$ cm^{-1}	$2·24 \times 10^{-2}$	$2·248 \times 10^{-2}$	1·004
$\mu\ \Omega^{-1}$ cm^2	1·077	1·082	1·004
$\mu\eta\ \Omega^{-1}$ cm^2 cP	10·95	10·51	0·959
D Volt	3·25(@ 10°)	2·5 (@ 0°)	—

greater, proportionately to its greater molecular weight, so that the two molar volumes are very similar. Likewise the apparent molar volume of co-ordinated boron trifluoride [$V_{complex} - V_{ligand}$] is almost the same in the two compounds.

The similarity in the viscosity and the conductivity has already been mentioned, the compounds differing notably only in the activation energy of viscous flow, which is 11 per cent greater for the complex with heavy water. The results imply that the approximate degree of ionic dissociation[5] ($\mu\eta$) in the two compounds is similar, the numerical value being 10–11 per cent. This deduction is in no way at variance with the recent investigation on boron trifluoride monohydrate by means of nuclear magnetic resonance,[6] which indicated that the structure of the slowly crystallized solid complex was unionized and best considered as $BF_3{\cdot}H_2O$. The phenomenon of a covalent solid melting to give an ionic liquid is not unknown, though it is less common than the related change from an ionic solid to a covalent liquid.[2]

Boron trifluoride monodeuterate is not a good compound on which to study the

[4] N. N. GREENWOOD *J. inorg. nucl. Chem.* **5**, 229 (1957).
[5] N. N. GREENWOOD and R. L. MARTIN *J. chem. Soc.* 1427 (1953).
[6] P. T. FORD and R. E. RICHARDS *J. chem. Soc.* 3870 (1956).

influence of supercooling on physical properties since it readily evolves boron trifluoride and is consequently difficult to purify as a stoichiometric compound. Nevertheless, it appears that the slope of the Arrhenius plot of specific conductivity increases discontinuously by 6·3 per cent on passing into the supercooled region; the corresponding viscosity plot is essentially linear throughout the whole temperature range studied. Alternatively, the viscosity results can be represented in terms of the equation $v = b + B\phi$, where v is the specific volume, b a constant, and ϕ the fluidity in cP^{-1}. The slope of the graph gives Batschinski's constant B which is related to the size of the kinetic units undergoing viscous flow.[7] This method is usually more sensitive to anomalies in the neighbourhood of the melting point than is the Arrhenius equation,[3] and indeed the present viscosity data show that B increases by 21·8 per cent at 10·5°, i.e. just below the m.p. The specific conductivity can be treated similarly by means of the equation $v = b' + B'\kappa$; there is a discontinuous increase in slope of 11·3 per cent on supercooling below 10°.

The main purpose of the present measurements was to obtain information on the properties of boron trifluoride monodeuterate before undertaking transport and diffusion experiments. The results of these tracer experiments will be published later. The present data are compared with those obtained on the dihydrate and dideuterate in the following paper and this enables some preliminary deductions to be made about the nature of the transport process in these liquids.

[7] A. J. BATSCHINSKI *Z. phys. Chem.* **84**, 643 (1913).

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J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 229 to 236. Pergamon Press Ltd., London

SOME PROPERTIES OF BORON TRIFLUORIDE DIDEUTERATE, $D_3O[BF_3 \cdot OD]$; THE VISCOSITY OF ISOTOPIC PAIRS OF LIQUIDS, AND THE MECHANISM OF ELECTRICAL CONDUCTION IN MOLTEN COMPLEXES

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(*Received* 24 *April* 1957)

Abstract—The melting point, density, viscosity, and electrical conductivity of the compound $BF_3.2D_2O$ are reported and compared with those of the dihydrate and the corresponding monohydrate and monodeuterate. The results are interpreted as suggesting that conduction occurs by ionic migration, rather than by a proton or deuteron switch mechanism.

THIS paper reports some properties of the 1:2 compound of boron trifluoride with heavy water. The experimental techniques used were the same as those outlined in the preceding paper.[1] From the results obtained, preliminary deductions may be made about the mechanism of transport of the electric current in these ionic melts.

RESULTS

Boron trifluoride dideuterate was prepared by absorbing the theoretical quantity of boron trifluoride in heavy water and then fractionally freezing the complex until a maximum m.p. had been obtained. During the preparation a white precipitate

TABLE 1.—DENSITY OF $D_3O[BF_3 \cdot OD]$ BETWEEN 8 AND 25°

$t°$	d_4^t
8·00	1·7114
10·00	1·7085
12·00	1·7056
14·00	1·7027
16·00	1·6999
18·00	1·6971
20·00	1·6940
25·00	1·6864
25·13	1·6862

formed which later redissolved in the manner already described for the normal hydrates.[2] The m.p. of the purified complex was 11·3° in agreement with the value

[1] N. N. GREENWOOD *J. inorg. nucl. Chem.* **5**, 224 (1957).
[2] N. N. GREENWOOD and R. L. MARTIN *J. chem. Soc.* 1915 (1951).

of 11·2° found recently by FORD and RICHARDS.[3] This is 5·1° above the melting point of the dihydrate, a difference which is larger than for any other deuterated compound reported in the literature.

The density of molten $D_3O[BF_3{\cdot}OD]$ between 8 and 25° is given in Table 1; the results, which have been corrected for buoyancy and for thermal expansion of the glass, may be expressed with an accuracy of 1 in 10^4 by the equation

$$d_4^t = 1{\cdot}7232 - 1{\cdot}46 \times 10^{-3}t.$$

The viscosity data are summarized in Table 2. They correspond to a mean activation energy for viscous flow of 5·05 kcal $mole^{-1}$. Above the melting point the

TABLE 2.—VISCOSITY OF $D_3O[BF_3{\cdot}OD]$ BETWEEN 7 AND 25°

t°	ν cS	η cP	ϕ cP^{-1}
7·43	6·14	10·52	0·0951
8·95	5·86	10·02	0·0998
10·02	5·67	9·67	0·1032
10·95	5·49	9·37	0·1068
11·62	5·38	9·18	0·1089
12·95	5·17	8·81	0·1135
13·85	5·00	8·51	0·1175
17·78	4·46	7·57	0·1321
20·00	4·22	7·15	0·1398
25·13	3·67	6·19	0·1615

slope is near to 4·92 kcal and this increases to about 5·17 in the supercooled region, but there are insufficient experimental points to decide whether this 5 per cent increase is discontinuous or not. These activation energies are appreciably larger than those for $H_3O[BF_3{\cdot}OH]$ (see Table 5) and, in addition, the numerical values of the viscosity of the deuterium compound are greater throughout the range studied.

The specific electrical conductivity of the dideuterate was found to be slightly dependent on frequency but the effect could be minimized if the cell constant was also

TABLE 3.—EFFECT OF FREQUENCY ON CONDUCTIVITY AT 25·13°

c/s	500	1000	2000	3000	5000
$10^3\kappa\ \Omega^{-1}\ cm^{-1}$	7·074	7·127	7·157	7·169	7·186

determined at the same frequency. The effect of frequency on the measured conductivity at 25·13°, using a constant value for the cell constant as determined at 1000 c/s with aqueous KCl-solution, is indicated in Table 3. Table 4 summarizes the temperature dependence of conductivity at 1000 c/s.

[3] P. T. FORD and R. E. RICHARDS *J. chem. Soc.* 3870 (1956).

The plot of log κ against $1/T°K$ is linear and leads to an activation energy of conduction of 3·97 kcal mole^{-1}. At 20° the conductivity is $6{\cdot}414 \times 10^{-2}$ Ω^{-1} cm^{-1}, a value which is about 9 per cent less than that obtained for the dihydrate; the molar conductivity (4·083 Ω^{-1} cm^2 mole^{-1}) is also less, since the molar volumes of the two

TABLE 4.—CONDUCTIVITY OF MOLTEN $D_2O[BF_2 \cdot OD]$ BETWEEN 8 AND 25°

$t°$	$10^2\kappa$ Ω^{-1} cm^{-1}	μ Ω^{-1} cm^2	$\mu\eta\Omega^{-1}$ cm^2 cP
7·70	4·760	3·000	31·3
8·80	4·906	3·095	31·2
9·95	5·058	3·194	31·0
11·15	5·198	3·285	30·6
13·12	5·467	3·461	30·2
14·98	5·712	3·622	29·8
17·40	6·049	3·844	29·4
19·85	6·396	4·073	29·2
21·30	6·570	4·188	28·9
25·13	7·127	4·559	28·2

complexes are the same. However, when allowance is made for viscosity, the reduced conductivity of the deuterium compound becomes very similar to that of the dihydrate and, in fact, is slightly the larger. The values listed in Table 5 suggest[4] that in both compounds the degree of ionic dissociation is about 30 per cent.

TABLE 5.—COMPARISON OF $H_2O[BF_2 \cdot OH]$ AND $D_2O[BF_2 \cdot OD]$ AT 20°

Property	$H_2O[BF_2 \cdot OH]$	$D_2O[BF_2 \cdot OD]$	Ratio D/H
Mol. wt. g mole^{-1}	103·85	107·88	1·040
m.p. °C	6·2	11·3	1·018
d_4^{20} g ml^{-1}	1·6320	1·6940	1·039
V_M ml mole^{-1}	63·62	63·68	1·001
V_M (BF_3) (apparent)	27·31	27·28	—
dd/dt g ml^{-1} deg^{-1}	$1{\cdot}31 \times 10^{-3}$	$1{\cdot}46 \times 10^{-3}$	1·015
ν cS	3·90	4·22	1·080
η cP	6·36	7·15	$1{\cdot}12_5$
ϕ cP^{-1}	0·157	0·140	0·891
B cP ml g^{-1}	0·118	0·137	1·16
E_η kcal mole^{-1}	4·1	5·05	1·24
E_κ kcal mole^{-1}	3·1	3·97	1·28
κ Ω^{-1} cm^{-1}	$7{\cdot}03 \times 10^{-2}$	$6{\cdot}41 \times 10^{-2}$	0·912
μ Ω^{-1} cm^2	4·47	4·08	0·913
$\mu\eta$ Ω^{-1} cm^2 cP	28·4*	29·2	1·028
D Volt	2·7	2·4 (at 23°)	0·89

* In Table 1 of reference 2 values of $\mu\nu$ were erroneously tabulated instead of $\mu\eta$ so that the reduced conductivities listed there are too small by a factor equal to the density. Thus, at 20°, $\mu\eta$ is not 17·4 Ω^{-1} cm^2 cP, but 28·4 Ω^{-1} cm^2 cP as given in the present table.

[4] N. N. GREENWOOD and R. L. MARTIN *J. chem. Soc.* 1427 (1953).

In a direct-current experiment at 23° the decomposition potential of $D_3O[BF_3{\cdot}OD]$ was found to be 2·4 V. Electrolysis liberated deuterium at the cathode and oxygen at the anode in the volume ratio 2:1. The back e.m.f. generated by these electrolysis products surrounding the electrodes was 2·3 V indicating the absence of any appreciable over-voltage in this instance.

The properties of boron trifluoride dihydrate and dideuterate at 20° are listed in Table 5 which summarizes the various comparisons alluded to above.

DISCUSSION

Viscosity of isotopic pairs of liquids

The viscosity results on the compounds of boron trifluoride with heavy water are of interest in being the only information available on the effect of deuterium substitution on the viscosity of an ionized liquid. Indeed, little is known about the viscosity of deuterium-containing compounds at all, the only previously investi-

TABLE 6.—EFFECT OF DEUTERIUM SUBSTITUTION ON VISCOSITY CHARACTERISTICS

Compound	$(M_D/M_H)^{\frac{1}{2}}$	t°C	η cP	Ratio D/H	E_η kcal mole^{-1}	Ratio D/H	Bml cP g^{-1}	Ratio D/H
H_2		−253°	0·0129		0·070		0·0254	
D_2	1·414	−253°	0·0418	3·24	0·110	1·57	0·0232	0·91
CH_4		−183°	0·210		—[a]		—[a]	
CD_4	1·118	−183°	0·234	1·113	—[a]	—	—[a]	—
H_2O		20°	1.005		4·17[b]		—[c]	
D_2O	1.054	20°	1.251	1.245	4.60[b]	1.10	—[c]	—
H_2O_2		20°	1·249		3·00[d]		0·0425[d]	
D_2O_2	1·030	20°	1·358	1·085	2·99[d]	0·997	0·0420[d]	0·99
$H[BF_3{\cdot}OH]$		20°	10·18		3·8		0·159	
$D[BF_3{\cdot}OD]$	1·011	20°	9·71	0·955	4·21	1·11	0·147	0·93
$H_3O[BF_3{\cdot}OH]$		20°	6·36		4·1		0·118	
$D_3O[BF_3{\cdot}OD]$	1·020	20°	7·15	1·122	5·05	1·24	0·137	1·16

[a] Viscosity known at one temperature only so that E_η and B cannot be computed.

[b] These values change rapidly with temperature from about 5 kcal mole^{-1} at 5° to about 3 kcal mole^{-1} at 100°; the ratio D/H varies from 1·14 to 1·04 in the same temperature range.

[c] Batschinski's equation does not apply because of the density anomaly in water (4°) and heavy water (11·2°).

[d] Calculated from two points only (0 and 20°) on the assumption that the relevant equations (Arrhenius and Batschinski) are applicable.

gated isotopic pairs being D_2/H_2,[5] CD_4/CH_4,[6] D_2O/H_2O,[7] and D_2O_2/H_2O_2.[8] The data on these compounds may be used to calculate the Arrhenius parameter E_η the equation $\eta = \eta_0 \exp(E_\eta/RT)$ and Batschinski's constant B in the equation $v = b + B\phi$, where η_0 and b are constants, v is the specific volume, and the other symbols have their usual meanings. When this is done (Table 6) several interesting points emerge.

[5] A. VAN ITTERBEEK and O. VAN PAEMEL *Physica* **7**, 208 (1940); **8**, 133, 522 (1941).
[6] S. E. BRESLER and A. LANDERMAN *J. exp. theor. Phys.* **10**, 250 (1940).
[7] R. C. HARDY and R. L. COTTINGTON *J. chem. Phys.* **17**, 509 (1949).
[8] M. K. PHIBBS and P. A. GIGUÈRE *Canad. J. Chem.* **29**, 173 (1951).

(1) Deuterium substitution may either increase or decrease the viscosity of a liquid. For the four covalent, molecular liquids mentioned the viscosity is increased; this is the expected direction of change since both mass and moment of inertia are increased, though it may be unwise to generalize from so few examples. The ratio of the viscosities of an isotopic pair of liquids will equal the square root of the ratio of the molecular weights provided:[9] (a) all the atomic masses are changed in the same ratio, or (b) the intermolecular potential is of a central-force type. Liquid hydrogen conforms to the first criterion, but the viscosity ratio (3·24) is much greater than the expected ratio (1·414) because of the supervention of quantum effects arising from the influence of the lower zero-point energy of deuterium at temperatures close to the absolute zero. Methane conforms to the second criterion and is, in fact, the only compound known for which the viscosity ratio (1.113) is the same as the square root of the mass ratio (1·118) to within the experimental error. For both water and hydrogen peroxide the viscosity ratio is larger than the square root of the mass ratio. This is understandable for, although deuterium-substitution in water (say) increases the molecular weight by only 11 per cent, the moment of inertia of the molecule is doubled. The large increase in viscosity is not due, as is sometimes stated, to an increase in the number of hydrogen-bonds in heavy water; detailed calculations have shown that the extent of hydrogen-bonding in heavy water is only 4 per cent greater than that in ordinary water at room temperature and that the degree of association is identical for the two liquids at 100°,[10,11] yet the viscosity of heavy water at 100° is still more than 15 per cent greater than that of its isotopic counterpart.

The viscosity of boron trifluoride monodeuterate is less than that of the monohydrate at temperatures above 17° and the same behaviour seems possible for the dideuterate, the extrapolated viscosity curve for which falls below that of the dihydrate at temperatures above 40°. The interpretation of this effect is not clear. Coulombic interaction between ions in these liquids is doubtless a complicating factor but it is hard to see how such interactions, of themselves, could lower the viscosity of the deuterium-substituted complexes. Below room temperature deuterium substitution increases the viscosity of both hydrates of boron trifluoride.

(2) The second point in Table 6 which calls for comment is the Arrhenius parameter E_η which is normally interpreted as an activation energy of viscous flow. Deuterium substitution appears always to increase the activation energy, the only exception being hydrogen peroxide where the two values of E_η are identical to within the experimental error. However, these values are based on data at two temperatures only and moreover, the peroxides are difficult to prepare in a state of high purity.

(3) The final quantity in Table 6 to be discussed is Batschinski's constant B. That this may be taken as roughly proportional to the size of the flow-units in a liquid has been well established both for molecular and ionic systems.[12, 13] The correlation is further confirmed in Table 6 from the similarity in the magnitude of B for each isotopic pair. This enables a significant deduction to be made about the nature of the ions present in the molten hydrates of boron trifluoride for the constant is *larger* for the monohydrate and monodeuterate than for the dihydrate and dideuterate. Only

[9] J. A. Pople *Physica* **19**, 668 (1953).
[10] A. Eucken *Z. Elektrochem.* **52**, 255 (1948).
[11] A. Gierer and K. Wirtz *Z. Naturf.* **5A**, 577 (1950).
[12] A. J. Batschinski *Z. phys. Chem.* **84**, 643 (1913).
[13] B. S. Harrap and E. Heymann *Chem. Rev.* **48**, 45 (1951).

two of the five formulations of these compounds mentioned in the preceding paper satisfy this condition, viz. (iii) and (iv) below:

	1:1 complex	1:2 complex
(i)	$BF_3.H_2O$	$BF_3.2H_2O$
(ii)	$H^+[BF_3{\cdot}OH]^-$	$H_3O^+[BF_3{\cdot}OH]^-$
(iii)	$[H_3O{\cdot}BF_3]^+[BF_3{\cdot}OH]^-$	$H_3O^+[BF_3{\cdot}OH]^-$
(iv)	$[(H_2O)_2BF_2]^+BF_4^-$	$[(H_2O)_2BF_2]^+F^-$
(v)	$H_2F^+[F_2B{=}{=}O]^-$	$H_2F^+[F_2B(OH)_2]^-$

Formula (iii) for the monohydrate is obtained by solvating the bare proton in formula (ii) by an undissociated molecule of the monohydrate and is the favoured scheme for ionization since formulae (iv) cannot readily account for the stoichiometric liberation of oxygen at the anode when the molten complexes are electrolysed. For each of the remaining schemes, (i), (ii), and (v), the Batschinski constant for the monohydrate would be *smaller* than that for the dihydrate. The viscosity results are thus entirely consistent with the deductions made earlier from electrolysis results on the complexes with ordinary water.[2]

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Mechanism of conduction

The specific conductivity of an electrolytic system is related to the number of ions per ml (n) and their mobility (u) by a formula of the type $\kappa = neu$, where e is the electronic charge. A knowledge of the ionic mobility, therefore, in conjunction with the specific conductivity, permits a direct determination of the number of ions present and hence the degree of ionic dissociation. It is the ultimate purpose of the present work to determine the necessary ionic mobilities by means of electrolytic transport measurements using deuterium as tracer and a detailed analysis of the conduction process in these melts must await such measurements. However, some preliminary deductions can be made from the results presented in this and the preceding paper.

In the absence of experimental values for the ionic mobilities, the percentage degree of ionic dissociation (α) of a compound may be calculated approximately by the expression:[4]

$$\alpha = \frac{M\kappa\eta}{d} \times \frac{100}{2Neu_0} = \mu\eta\left(\frac{100}{2Neu_0}\right)$$

In this equation N is Avogadro's number and u_0 is a standard reference mobility in a medium of viscosity 1 cP. When u_0 is given the plausible value of 5×10^{-4} cm^2 sec^{-1} V^{-1}, the term in parentheses becomes numerically equal to unity so that the degree of ionic dissociation is given by the reduced conductivity $\mu\eta$. The whole argument turns on the assumption that the ionic mobility is viscosity controlled; should the mobility be abnormally high (as for the HSO_4^- ion in sulphuric acid) then the calculation would require modification, perhaps by as much as a factor of 5–10. It therefore becomes of prime importance to decide whether the ions move with the normal Stokes mobility or whether conduction occurs by a proton switch mechanism followed by ionic reorientation.

The possibility of a switch mechanism in molten boron trifluoride monohydrate cannot be rejected out of hand because of the formal similarity of this compound to sulphuric acid (sulphur trioxide monohydrate). However, a comparison of the

conductivities of the hydrates of boron trifluoride with those of the deuterates shows that such a mechanism is most unlikely, for, if a proton or deuteron switch did occur, then either (a) the jump frequency or (b) the speed of subsequent rotation of the ion into another favourable orientation must be the rate-determining process. Neither of these hypotheses fit the observed facts and hence conduction cannot be by a switch mechanism. This can be seen in the following way:

(a) If the jump frequency were rate-determining, then the deuteron mobility should be less than the proton mobility by a factor $\sqrt{2}$ as indeed it is in water itself.[14] When actual conductances are compared, rather than the mobility of the anomalous ion, allowance must also be made for the normal Stokes mobilities of the ions, but as these are considerably less than the switch mobility, the ratio is only slightly below the expected value. For example the ratio of the anomalous mobility of the hydrogen ion in water to that of the deuterium ion in heavy water is 1·43 whereas the ratio of the limiting conductance of HCl in water to that of DCl in heavy water is 1·37 at 25°. By contrast, reference to Table 3 in the preceding paper and to Table 5 in this paper shows that the conductivities of the deuterium substituted compounds are very similar to those of the proton-containing complexes; the ratio of either the specific or the molar conductivity of the monohydrate to that of the monodeuterate is 1/1·004, i.e. 0·996, and the corresponding figure for the dihydrate and dideuterate is 1·095. It must be concluded that proton or deuteron jump-frequency is not the rate-controlling process; hence if the postulate of a proton or deuteron switch mechanism is to be retained then speed of reorientation of the ions must be the rate-controlling process.

(b) However, speed of ionic reorientation into another favourable position after a jump cannot be rate-determining in these complexes since to be so, ionic rotation must be slower than the hypothetical jump frequency. From the theory of dielectric relaxation,[15] the relaxation time (τ), which is an indication of the time required for reorientation by rotation, is given approximately by the expression $\tau = 3\eta V/RT$, where V is the hypothetical volume of 1 mole of molecules. For an order-of-magnitude calculation this volume can be set equal to the molar volume and the viscosity η equated to the bulk viscosity. Substitution of numerical values for boron trifluoride dideuterate at room temperature gives $\tau = 5 \times 10^{-10}$ sec, and the other complexes have very similar values. On the other hand, the mean distance of the postulated proton or deuteron jump is about one ionic diameter so that, from the values of the conductivities, the excess jump frequency in the direction of the field is of the order of 5×10^{-4} sec, which is a millionfold slower than the speed of reorientation. Thus, there should be ample time for reorientation after each hypothetical jump in the direction of the field; in other words ionic rotation is not the rate-determining process in these liquids.

In this way it is concluded that a switch mechanism followed by rotation cannot account for the observed similarity in conductivity of the isotopic pairs of hydrates. Conduction by normal ionic migration is therefore the more probable mechanism and consequently the reduced conductivity should give a correct indication of the extent of ionic dissociation. Further, it follows that deuterium substitution has little effect on the degree of ionic dissociation; both the monohydrate and monodeuterate are dissociated to the extent of about 10 per cent and the figure for the dihydrate and

[14] A. Gierer and K. Wirtz *J. phys. Chem.* **56**, 914 (1952).
[15] C. P. Smyth *Dielectric Behaviour and Structure*. McGraw-Hill, New York (1955).

dideuterate is about 30 per cent. Since no allowance has been made for electrostrictive effects which will doubtless occur at such high ionic concentrations, these figures probably represent lower limits. The maximum value for the monohydrate and monodeuterate is 50 per cent as these compounds are formulated as $[BF_3,H_2O{\cdot}H]^+$ $[BF_3{\cdot}OH]^-$ and $[BF_3,D_2O{\cdot}D]^+[BF_3{\cdot}OD]^-$. The maximum value for the 1:2 complexes is 100 per cent. The results therefore suggest that both sets of complexes are virtually completely ionized according to scheme (ii) above but that ionic dissociation into kinetically free ions is somewhat restricted by ion-pair formation.

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SEPARATION OF THORIUM AND RARE-EARTH ELEMENTS IN NITRIC ACID MEDIA BY ANION EXCHANGE

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Abstract—The distribution coefficients of thorium and praseodymium between Dowex-1 and aqueous nitric acid have been determined. Separations between thorium and the rare-earth elements are described.

IN A recent communication[1] we described the adsorption of thorium by anion-exchange resins from nitric acid media. Subsequently, the possible utilization of this result for the separation of thorium and the rare-earth elements was investigated, and the results obtained form the basis of this paper.

EXPERIMENTAL

The adsorbabilities were investigated with Dowex-1, 8 per cent DVB, 50–100 mesh. ^{234}Th (β_γ, 24·1 days period) and ^{143}Pr (β, 13·7 days period) were used as tracers in this study. ^{234}Th was extracted from uranyl nitrate according to the procedure of DYRSSEN[2] and ^{143}Pr was obtained from the "Service de Radioéléments Artificiels du CEA" in France.

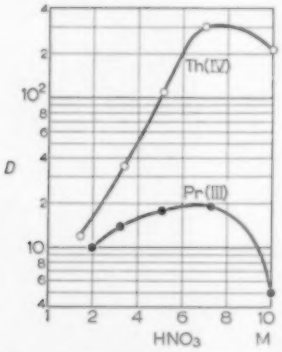

FIG. 1.—Distribution coefficients for thorium and praseodymium.

The values of the distribution coefficients D (amount of radio-element/g of dry resin divided by the amount of radio-element per ml of solution) were obtained by the equilibrium method. Measured amounts of the resin and the solution were agitated until the equilibrium was attained (approximately 24 hr). After centrifuging, an aliquot was evaporated and its activity measured with a Geiger-Müller counter.

Separation of ^{234}Th and ^{143}Pr was investigated in 1 cm^2 × 5 cm Dowex-1 columns which had been pretreated with appropriate HNO_3 solution. Elution of the radio-elements was followed by sampling the effluents in volumes of 2 ml, which were evaporated and counted. The extent of separation was determined by radiation absorption measurements.

[1] J. DANON *J. Amer. chem. Soc.* **78**, 5953 (1956).
[2] D. DYRSSEN *Svensk kem. Tidskr.* **7**, 153 (1950).

Separation of macro amounts of Th from μg of rare earths was investigated in columns made from the same resin. Solutions containing μg of Ce, La, Nd, Eu, Sm and Y were prepared by dissolution of the respective oxides (Johnson, Matthey "Specpure") in nitric acid. Elution was carried out as previously and the effluent was analysed radiometrically for Th and colorimetrically for the rare earths using sodium alizarin sulphonate.[3] In our experiments the optical density of the solution was determined at 525 mμ using a Beckman DU quartz spectrophotometer. All experiments were carried out at room temperature.

RESULTS

Fig. 1 illustrates the effect of increasing HNO_3 concentration on the values of the distribution coefficients for ^{234}Th and ^{143}Pr.

It can be seen that the adsorbability of both elements first increases with the HNO_3

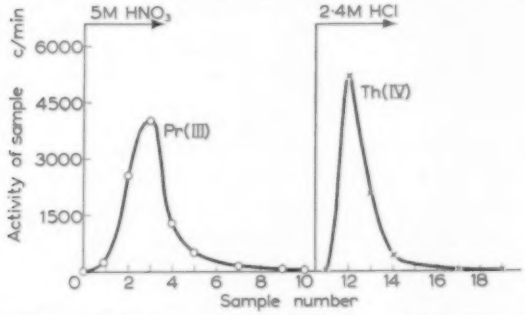

FIG. 2a.—Elution of praseodymium and thorium from Dowex-1.

molarity, reaches a maximum near 7 M HNO_3, where D $\sim$300 for Th and D $\sim$20 for Pr, and then decreases with further increase in the acid molarity.

In a first series of experiments we investigated the separation of trace amounts of

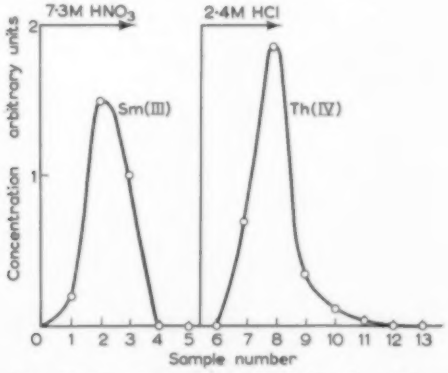

FIG. 2b.—Elution of samarium and thorium from Dowex-1.

Th(IV) and Pr(III). In a typical experiment 2 ml of a 5·0 M HNO_3 solution containing ^{234}Th and ^{143}Pr was added to a 1 cm^2 $\times$ 5 cm column, pretreated with 5·0 M HNO_3. Elution was carried out with acid of the same molarity at a flow rate of 0·4 ml/min and the effluent was analysed radiometrically. ^{143}Pr was completely removed from the resin with approximately 3 column volumes of the HNO_3 solution, while ^{234}Th was retained on it and was eluted with 2·4 M HCl (Fig. 2a).

[3] E. B. SANDELL *Colorimetric Determination of Traces of Metals.* Interscience, New York (1950).

Fig. 2b illustrates the results obtained in the separation of milligram amounts of Th(IV) from micrograms of Sm(III). In this experiment 3 ml of a 7·3 M HNO_3 solution containing 40 mg of $Th(NO_3)_4$ and 100 μg of Sm was added to a 1 $cm^2 \times 7$ cm column of Dowex-1. Sm(III) was removed with 7·3 M HNO_3 from Th(IV); the latter remained on the column and was eluted with 2·4 M HCl. Experiments with La(III), Nd(III), Eu(III) and Y(III) showed that these metals are readily removed from the column with 5–8 M HNO_3 and for this reason they can easily be separated from Th(IV). Complete separation between Th(IV) and Ce(IV) in HNO_3 media cannot be achieved in a single pass through the column since Ce(IV) is also adsorbed under these conditions. The addition of hydrogen peroxide to the HNO_3 solution considerably reduces the adsorbability of Ce, suggesting that Ce(III), like the other trivalent rare-earth nitrates, is only slightly adsorbed.

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PAPER CHROMATOGRAPHIC ANALYSIS OF IRRADIATED URANIUM IN A HYDROFLUORIC ACID MEDIUM

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Abstract—Chromatographic papers have been found compatible with aqueous hydrofluoric acid developing solutions to approximately 60 per cent by weight of the acid. Hydrofluoric acid is also an important solution and complexing medium in the processing and analysis of certain irradiated targets and fissile materials. The aqueous-hydrofluoric acid and methyl ethyl ketone-hydrofluoric acid media have proved to be a very convenient and versatile system in the isolation of carrier free isotopes and in the analysis of irradiated materials. The complete or partial separations of twelve fission and neutron capture isotopes of irradiated uranium are described. The identification of the isotopes has been made in most cases with a 256 channel scintillation spectrometer.

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THE analysis of irradiated targets by paper chromatographic methods offers an exceptionally simple but versatile analytical method. Fractions developed in the paper are in a convenient form for rapid mounting and counting. When the fractions are counted with a scintillation spectrometer, a quantitative analysis of a relatively large number of components can be made on a single chromatogram.

This investigation has been arbitrarily restricted to the technique referred to as ascending linear paper chromatography,[1] and to the use of solvents containing hydrofluoric acid. The application of methyl ethyl ketone and hydrofluoric acid solvent mixtures to this technique was made by HUNT and WELLS[2] for the separation of niobium in low grade ores, by FUDGE and WOODHEAD[3] for the isolation and determination of protactinium, and by FUDGE[4] for the determination of niobium in fission products.

EXPERIMENTAL

The papers found applicable were ½ in. wide Whatman 3-MM paper strips or Whatman No. 1 and No. 2 paper strips. The papers were not pre-treated.

Experiments were run in closed polythene cylinders with the paper centred at the top by a split cork stopper. At the bottom of the strip the paper was centred by a flat platinum spline inserted perpendicular to the plane of the paper before placing in the cylinder. When the paper was in position, the spline was below the developing solution surface, and the original sample spot about 2·0 cm above the surface. The free volume of the polythene cylinders was relatively small: 29 mm diameter by 30 cm. With proper lighting, the solvent boundary was visible through the polythene. The atmosphere was saturated with solvent vapours by wetting the walls with the solvent just before introducing a strip into the vessel. If larger vessels are used, considerable care must be taken to obtain an atmosphere saturated with the solvent vapours.

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[1] H. H. STRAIN, T. R. SATO and J. ENGELKE *Analyt. Chem.* **26**, 90 (1954).
[2] E. C. HUNT and R. A. WELLS *CRL/AE*-113 (1954).
[3] A. J. FUDGE and J. L. WOODHEAD *AERE/C/R*-1501 (1954).
[4] A. J. FUDGE *AERE/C/R*-1502 (1954).

Otherwise the zones with relatively low R_F(*) values continue to move because of solvent evaporation, while the solvent front slows down.

The behaviour of the various fission products was studied by irradiating samples of highly purified U_3O_8 in a CP—5 flux of 10^{13} n/cm^2 sec for 1 hr and 1 week. Analyses of the irradiated uranium were made after 24 hr cooling and after 1 week's cooling, respectively. Also a Chalk River uranium sample irradiated in the maximum flux for approximately 1 year and cooled for 2 years was chromatographed. The movement of individual isotopes was studied by employing the chemically purified fission products. Other isotopes employed were technetium-95 prepared by deuteron bombardment of molybdenum, and the radioactive nuclides obtained by the (n, γ) reactions on the natural isotopic mixtures of cerium, molybdenum, antimony, tellurium, and caesium.

In this investigation, it was not considered feasible to develop the complete working details of individual fission-product procedures. The objects were to identify the elements in the paper, the valence states of the species, and their R_F values when developed by the various hydrofluoric acid–methyl ethyl ketone solutions. One possible limitation of such a multi-component analysis on a single sample appeared to be the adjustment of the valence states of the elements involved, but no serious difficulty in this respect was encountered. The highest stable valence states formed the species with the highest R_F values in most cases.

The irradiated uranium oxide was dissolved with concentrated nitric acid in a platinum casserole. A small crystal of ammonium iodide was added to aid in the elimination of the iodine fission products during dissolution. The sample was evaporated to dryness with a small amount of concentrated nitric acid under an infra-red lamp and finally dissolved in concentrated hydrofluoric acid. Complete conversion of the nitrates to fluorides was accomplished by two successive evaporations with small amounts of concentrated hydrofluoric acid followed by solution of the residue in dilute 1 : 3 hydrofluoric acid. Ten to twenty-five μl of this solution were then placed as a 5–10 mm circle on Whatman paper strips and were air dried. The sample spots were not allowed to spread to the edge of the paper. The valence states of neptunium and plutonium after dissolution are probably 5 and 4, respectively. There was no indication of multi-valence states forming more than one band for either element in the chromatograms.

The remaining elements were easily adjusted to their highest stable valence in the hot nitric acid, except cerium and americium, which remained in the trivalent states and showed no appreciable movement in any of the fluoride media.

Counting was done with a methane flow-type proportional counter, with a sodium iodide thallium activated well-type counter, and with the Argonne 256 channel magnetic-core-pulse height analyser.[5] The latter was associated with a 4 in. × 4 in. diameter cylindrical sodium iodide thallium activated crystal. The major portion of the identification of the various radioactive nuclides was made with the latter instrument by the observation of the γ-ray spectrum and the half-lives of the various full energy peaks. Table 1 contains the nuclear data employed. In addition, individual chromatograms were prepared with the various nuclides purified by the standard

* R_F is defined as the ratio of the distances of the solute frontal boundary and the solvent boundary, both as referred to the original sample position.

[5] R. W. SCHUMANN and J. P. MCMAHON *Rev. sci. Instrum.* **27**, 675 (1956).

TABLE 1.—NUCLIDES AND RADIOACTIVE DECAY DATA IDENTIFIED IN THE CHROMATOGRAMS

Nuclide	Gamma spectrum (keV)	Beta max. keV	Half-life	Remarks
Caesium-137 and barium-137m	661		32·6 years 156 sec	32 keV *K*-conversion from ^{137}Ba
Cerium-141	142		33 days	36 keV *K*-conversion from ^{141}Pr
Barium-140	537, 165, 30		12·8 days	^{140}La daughter
Niobium-97*m* and 97	750 660		60 sec 74 min	
Zirconium-97	(See ^{97m}Nb)		17 hr	
Tellurium-132	230 265*		77 hr	27 keV *K* conversion from ^{132}I
Strontium-90	No γ	610	28 years	
Yttrium-90	No γ	2200	64 hr	
Molybdenum-99	0·728, 181		67 hr	(See ^{99m}Tc)
Technetium-99*m*	142		6·0 hr	
Neptunium-239	106, 230 276, 323		2·3 days	106 keV most intense peak
Plutonium-239	17·8 *L*-conversion 53 and 100 (weak)		24,300 years	
Americium-241	59·8		470 years	32 keV escape peak
Protactinium-233	312 98		27 days	
Thorium-234	90 16 *L*-conversion		24 days	
Ruthenium-106	No γ	very weak	1·0 year	(See ^{106}Rh)
Rhodium-106	513 624 1·04	3500	30 sec	
Niobium-95	755	160	35 days	
Zirconium-95	730	371	65 days	

* Decay period of 77 hr found for both 230 and 265 keV peaks, latter peak has not been associated with ^{132}Te in the literature.

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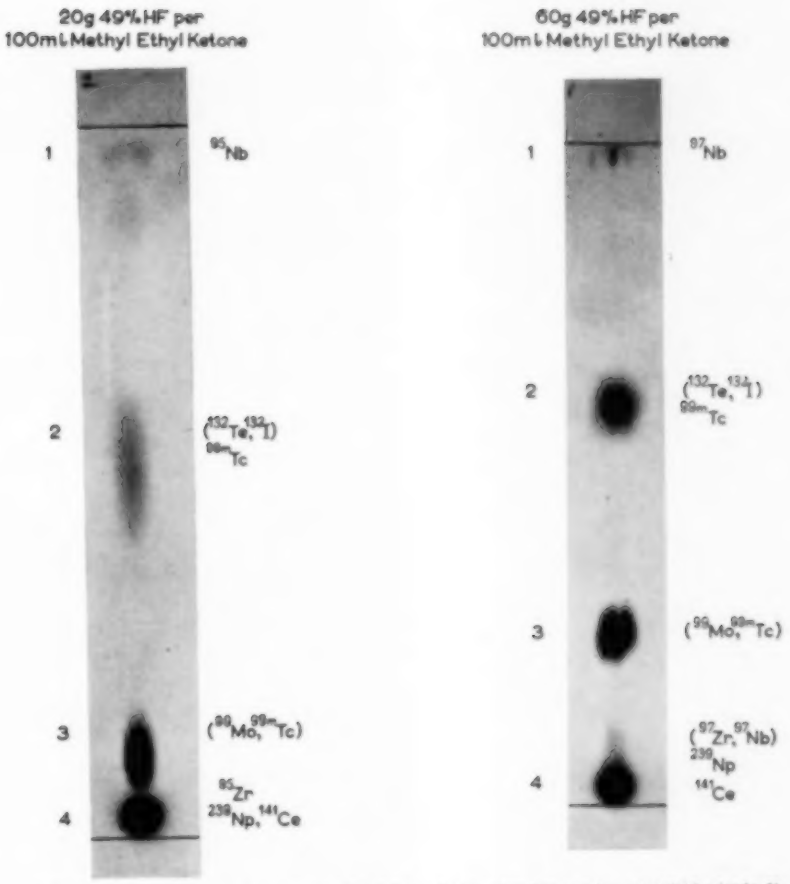

FIG. 1.—Uranium irradiated 1 hr in CP-5 flux of 10^{13} n/cm² sec and cooled 24 hr (strip 1) and 98 hr (strip 2) before chromatographing.

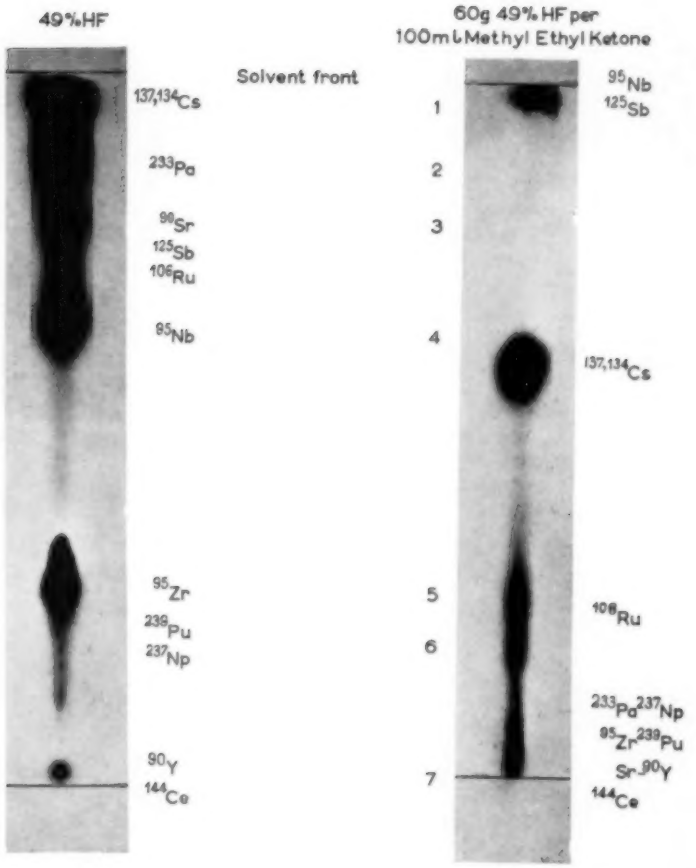

FIG. 2.—Chalk River uranium sample irradiated to 10 per cent total uranium atom burn-up and with 2 year cooling period.

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radiochemical procedures. The beta background was eliminated in the scintillation counting with beryllium metal absorbers.

Some of the paper strips, after chromatogram development, were dried, and a radio-autograph obtained (Figs. 1 and 2) by exposing a film strip in contact with the paper for 4–12 hr. Strips were also sealed between plastic tape, cut into 5 mm sections, and then counted in the well-type scintillation counter or the methane flow counter, and the various fronts located. Isotopes which had low intensity gamma branches or no gamma activity, such as strontium-90 and yttrium-90, were counted with the methane flow proportional counter.

DISCUSSION

Radio-autographs of three irradiated uranium samples are shown in Figs. 1 and 2. Fig. 1 shows the chromatograms of relatively green fission products of irradiated uranium. The chromatogram in Fig. 1 developed with 60 g 49 per cent hydrofluoric acid per 100 ml of methyl ethyl ketone was prepared with a uranium oxide sample irradiated in the maximum flux of CP-5 for 1 hr and cooled for 24 hr. The gamma spectra of the chromatographed original spot initially contain neptunium-239 as the overwhelmingly prominent activity. Zirconium-97 activity has streamed out just above the original sample spot with niobium-97 appearing as secular equilibrium is restored. Above the original sample spot in position three, molybdenum-99 is quite free of other activity in the relatively low level irradiated samples. Technetium-99 appears as secular equilibrium is restored. Ruthenium-103 and -106 from a longer irradiation may appear in this position as shown in Fig. 2. The behaviour of ruthenium was consistent only with oxide or metal samples dissolved and prepared according to the procedure previously outlined. Position 2 in Fig. 1 contained the 142 keV line of technetium-99 which decayed out completely with a 6 hr half-life and showed no evidence of 67 hr molybdenum-99. Tellurium-132 and its daughter, iodine-132, were also present in position 2. At low fluoride concentration, there was a tendency for tellurium to chromatograph in two positions. In Fig. 1, the very light spot below the niobium-95 activity was shown to be pure tellurium-132 at approximately 1/30 the total sample content. The alkali and alkali earth radioactive species, especially in the carrier-free state, showed a tendency under certain conditions to become immobile in the paper with the solvents employed. This was not appreciable with samples air dried at the original sample spot. However, in two-dimensional chromatograms the alkali or alkali earth species split into two fractions with the second developing solvent, one mobile, with the expected R_F value, and one immobile. The same effect could be obtained by re-wetting the dried original spot with hydrofluoric acid. Solutions which are incompletely converted to the fluoride salts or complexes may exhibit variable R_F values. However, the most noticeable effect in this case was a marked increase in the tailing of the various species. The behaviour of caesium fluoride solutions prepared by dissolution of caesium-137 amalgam in hydrofluoric acid was identical with solutions prepared from the nitrate salts by the procedure previously given.

Sodium-22 tracer was observed to chromatograph with the R_F values shown in Table 2 for caesium. Solutions with large quantities of ammonium or other alkali ion salts will overload the paper with resulting poor separations. Fig. 2 shows two chromatograms of a highly irradiated and 2 year old Chalk River uranium sample.

TABLE 2.—SUMMARY OF THE BEHAVIOUR OF RADIOACTIVE NUCLIDES WITH HF AND HF—MEK* MEDIUM IN ASCENDING PAPER CHROMATOGRAMS

Nuclide	R_f			Remarks
	20 g 49% HF per 100 ml MEK	60 g 49% HF per 100 ml MEK	49% HF	
^{137}Cs, ^{134}Cs	0·3	0·6	1·0	Other alkali and alkali earths behave similarly. Results may be difficult to reproduce as there is a tendency for a fraction to remain fixed in paper.
^{140}Ba	0·0	0·0	0·8	
^{90}Sr	0·0	0·0	0·8	
^{141}Ce, ^{140}La, ^{90}Y, ^{234}Th	0·0	0·0	0·0	
^{95}Nb, ^{97}Nb	1·0	1·0	0·7	
^{181}Ta	1·0	1·0	0·7	
^{95}Zr, ^{97}Zr	0·0	0·05	0·2	
$^{125}Sb(V)$	1·0	1·0	0·8	
^{106}Ru	—	0·2	0·8	Species unpredictable, variable R_F values
$^{132}Te(VI)$	0·5	0·6	0·8	
^{99}Mo	0·1	0·25	0·7	
^{99m}Tc	0·5	0·6	0·7	
^{233}Pa	0·0	0·05	0·9	
UO_2++	0·0	0·05	0·8	Considerable tailing
^{239}Np	0·0	0·0	0·2	Considerable tailing
^{239}Pu	0·0	0·0	0·2	Considerable tailing
^{241}Am	0·0	0·0	0·0	

* MEK = methyl ethyl ketone

The per cent total uranium atom burn-up of this sample was approximately 10 per cent. Protactinium-233, daughter of neptunium-237, was easily recognized. Irradiated thorium samples chromatographed with the two solvents of Fig. 2 gave the same R_F values for protactinium-233. Antimony(III) showed zero R_F in all fluoride media employed, and antimony(V) chromatographed with niobium(V) in the methyl ethyl ketone hydrofluoric acid media.

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 245 to 248. Pergamon Press Ltd., London

THE PARTIAL RESOLUTION OF CERTAIN INNER COMPLEXES BY MEANS OF A CHROMATOGRAPHIC TECHNIQUE

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(*Received* 8 *May* 1957)

Abstract—Adsorption of chromium(III) or cobalt(III) acetylacetonate on a column of D-lactose hydrate followed by elution with *n*-hexane-benzene or petroleum ether-benzene effects partial resolution into optically active fractions. Complete recovery of solute characterizes both systems. The same technique yields only optically inactive fractions with iron(III), gallium(III), and indium(III) acetylacetonates.

OCTAHEDRAL inner complexes of 1,3-diketones with tripositive metal ions are asymmetric in the solid state. If rearrangement of the chelated groups is sufficiently slow when the complex is dissolved, such a complex should thus be resolvable. However, such compounds are non-electrolytes and are thus not amenable to study by techniques involving diastereoisomers. Based upon the concept that the activities of the D- and L- forms of such an assymmetric species are unequal in a saturated solution containing an added optically active ion,[1] DWYER and GYARFAS[2] effected partial resolution of cobalt(III) and chromium(III) acetylacetonates by adding D- or L-tris(ethylenediamine)-cobalt(III) iodide to their solutions in ethanol and salting out with ammonium chloride at 4°. Selective adsorption on an optically active adsorbent is another approach to resolution of chelates of this type. Both optically active quartz[3–6] and starch[7–9] have been utilized to effect partial resolution of a number of complexes but not of species of the type considered here.

The authors have found that an extension of the procedure of HENDERSON and RULE[10,11] with D-lactose hydrate as adsorbent and *n*-hexane-benzene or petroleum ether-benzene as eluant effects partial resolution of cobalt(III) and chromium(III) acetylacetonates.

EXPERIMENTAL

Materials. Since the adsorbing power of either Merck U.S.P. or B. and A. Reagent Grade D-lactose hydrate was found to be unaltered by the purification procedure of HENDERSON and RULE,[11] these reagents were used as obtained from freshly-opened bottles, after being screened to −100 mesh. For some experiments, the adsorbent was

(1) F. P. DWYER, E. C. GYARFAS, and M. F. O'DWYER *Nature, Lond.* **167,** 1036 (1951).
(2) F. P. DWYER and E. C. GYARFAS *Ibid.* **168,** 29 (1951).
(3) R. TSUCHIDA, M. KOBAYASHI and A. NAKAMURA *J. chem. Soc. Japan* **56,** 1339 (1935).
(4) G. KARAGUNIS and G. COUMOULOS *Nature, Lond.* **142,** 162 (1938).
(5) G. K. SCHWEITZER and C. K. TALBOTT *J. Tenn. Acad. Sci.* **25,** 143 (1950).
(6) D. H. BUSCH and J. C. BAILAR, JR. *J. Amer. chem. Soc.* **76,** 5352 (1954).
(7) H. KREBS and R. RASCHE *Z. anorg. Chem.* **276,** 236 (1954).
(8) H. KREBS, R. RASCHE, A. J. WAGNER and J. DIEWALD *Angew. Chem.* **66,** 329 (1954).
(9) H. KREBS, J. DIEWALD and A. J. WAGNER *Ibid.* **67,** 705 (1955).
(10) G. M. HENDERSON and H. G. RULE *Nature, Lond.* **141,** 917 (1938); **142,** 163 (1938).
(11) G. M. HENDERSON and H. G. RULE *J. chem. Soc.* 1568 (1939).

first dehydrated at 125–135°. No significant difference between the hydrated and dehydrated forms was detected. All other chemicals and solvents were of analytical reagent quality. Benzene was dried over sodium wire and *n*-hexane and petroleum ether over anhydrous magnesium sulphate. Acetylacetone was redistilled just prior to use.

Chromium(III) acetylacetonate was prepared by treating the freshly precipitated hydrous oxide with excess acetylacetone and crystallizing from benzene by adding low-boiling petroleum ether. M.P. 215°:(Found: C, 51·96; H, 6·26. Calc. for $Cr(C_5H_7O_2)_3$: C, 51·57; H, 6·06). Cobalt(III) acetylacetonate was prepared by the slow addition of sodium hydroxide to an aqueous solution of cobalt(II) chloride, acetylacetone, and hydrogen peroxide. It was recrystallized from 95 per cent ethanol. (Found: C, 50·31; H, 5·73. Calc. for $Co(C_5H_7O_2)_3$: C, 50·57; H, 5·94.) Iron(III) acetylacetonate was prepared as outlined by HANTZSCH and DESCH.[12] M.P.180–183°: (Found: C, 51·22; H 6·36. Calc. for $Fe(C_5H_7O_2)_3$: C, 51·01; H, 5·99). Gallium(III) acetylacetonate was obtained by adding acetylacetone dissolved in dioxane to an aqueous gallium(III) sulphate solution and then making alkaline with aqueous ammonia. M.P. 195–196°, after drying over magnesium perchlorate. (Found: C, 49·16; H, 5·79. Calc. for $Ga(C_5H_7O_2)_3$: C, 49·08; H, 5·77.) Indium(III) acetylacetonate was obtained similarly and was recrystallized from benzene. M.P.186–189°: (Found: C, 44·10; H, 4·98. Calc. for $In(C_5H_7O_2)_3$: C, 43·72; H, 5·14).

Procedure. A 100 cm column of 2 cm diameter, equipped with a stopcock and a capillary bore drip-tip and with a plug of glass wool to retain the adsorbent, was two thirds filled with solvent. A thin slurry of adsorbent in the solvent was poured into the column in batches, with provision for settling between batches and removal of excess solvent through the stopcock. The column was tapped gently during filling to ensure uniformity. Adsorbent beds varied in length from 78 to 90 cm. Sufficient solvent was always left in contact with the adsorbent to prevent drying and consequent channelling.

Prior to an adsorption-desorption study, solvent was drawn through the adsorbent and read in the polarimeter to serve as a blank and to ensure the absence of soluble optically active substances. Solvent was then withdrawn until the top of the adsorbent bed just broke the surface of the liquid. A solution of the chelate in the same solvent was run on the surface of the adsorbent without disturbing that surface. The column was allowed to drain at a predetermined rate, and the eluting solvent was added when the adsorbent just broke through the solution surface. Elution was then continued at a fixed rate, and eluate fractions were collected as desired. Breakthrough was established by visual examination or, for the colourless samples, by spot-testing for acetylacetonate with iron(III) chloride solution. Representative data for typical experiments are summarized in Table 1.

RESULTS AND DISCUSSION

Partial resolution of both the chromium(III) and cobalt(III) chelates was effected, but only optically inactive fractions were obtained with the other chelates. The laevo-rotatory form of chromium(III) acetylacetonate is the more strongly adsorbed by D-lactose hydrate, but it is removed from the column after the dextro-rotatory form has been eluted. Fractions ranging in molecular rotation from +23,000° to

[12] A. HANTZSCH and C. H. DESCH *Liebigs Ann.* **323**, 1 (1902).

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TABLE 1.—CHROMATOGRAPHIC DATA FOR ADSORPTION AND ELUTION OF VARIOUS COMPLEXES

Chelate	Quantity taken (g)	Quantity recovered from eluate (g)	Adsorbent	Solvent and eluant	Observations
$Cr(C_5H_7O_2)_3$	0·115	0·1125	D-lactose hydrate	*n*-hexane-benzene (1:1)	Elution rate 6 drops/min Column length 78 cm
	0·0388	0·0358	D-lactose hydrate	*n*-hexane-benzene (1:1)	Elution rate 10 drops/min Breakthrough in 7 hr Column length 78 cm
$Co(C_5H_7O_2)_3$	0·0328	0·0305	D-lactose hydrate	petroleum ether-benzene (1:1)	Column length 90 cm
$Fe(C_5H_7O_2)_3$	0·0967	0·0927	D-lactose hydrate	*n*-hexane-benzene (1:1)	Elution rate 12 drops/min Breakthrough in 8 hr Column length 85 cm
$Ga(C_5H_7O_2)_3$	1·17	—	D-lactose	*n*-hexane-benzene (1:1)	Elution rate 8 drops/min Breakthrough in 11 hr Column length 81 cm
$In(C_5H_7O_2)_3$	1·512	—	D-lactose	*n*-hexane-benzene (1:1)	Elution rate 6 drops/min Breakthrough in 10½ hr Column length 79 cm

All optical measurements were made with a Schmidt and Haensch polarimeter (No. 9143). Data were obtained at 25° with 101 mm tubes. All measurements were at 5893 Å, except those for the cobalt compound where the wavelength was 5463 Å. Each reading was reproducible to ±0·003°.

−12,000° resulted. Racemization in the *n*-hexane-benzene solvent was 50 per cent complete at ca. 25° in ca. 8 days. With cobalt(III) acetylacetonate, the dextro-rotatory form is the more strongly adsorbed by D-lactose hydrate, but this form is eluted after the laevo-rotatory form has been removed. Fractions varying in molecular rotation from −57,000° to +50,000° were obtained. No racemization was detectable in the petroleum ether-benzene solvent in 2 days at ca. 25°. Elution of the two chelates from the adsorbent was quantitative.

Under the conditions employed, resolution of the chromium and cobalt compounds was undoubtedly fractional. This is clearly indicated by comparison of the maximum

molecular rotation obtained for the cobalt compound with the −107,000° obtained at 5461 Å for an admittedly optically impure product.[2] The success reported in the preparation of optically pure isomers by adsorption techniques[7–11] suggests, however, that refined procedures may lead to complete resolution of acetylacetonates by this procedure. The stabilities of the chromium and cobalt compounds toward racemization impose no critical time limitations on the procedure.

Failure to resolve the iron(III), gallium(III), and indium(III) compounds is in accord with general observations on the absence of optical isomerism in other potentially asymmetric chelates derived from these cations. It is indicative of much weaker bonding in these species than in the chromium(III) and cobalt(III) analogs. It is pertinent that DWYER and GYARFAS also were unable to resolve iron(III) acetylacetonate.[2]

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LETTERS TO THE EDITORS

Retention and radiolysis of some chromates

(*Received* 26 *June* 1957)

In an attempt to discover some of the factors determining the retention of the activity, after the neutron irradiation of solid substances, a comparison of the retention and radiation decomposition of some chromates has been made. It has been shown[1] that the retention in neutron-irradiated potassium chromate increases with the time of irradiation in the pile or on re-irradiation with an ionizing radiation. It seemed possible that this effect might be related to the concurrent radiolysis of the target material. Previous work[2] has shown that potassium dichromate exhibits quite a different retention from potassium chromate. Potassium chromate, dichromate, trichromate, and chromic anhydride were chosen, therefore, for comparison.

Code	Compound	Time of irradiation	Average mole % trivalent Cr	Average retention
Blank	K_2CrO_4	0	0·04	—
^{52}Cr	K_2CrO_4	2 weeks	0·02	73·4
^{51}Cr	K_2CrO_4	6 weeks	0·03	77·2
Blank	$K_2Cr_2O_7$	0	0·02	—
^{52}Cr *B*	$K_2Cr_2O_7$	2 weeks	0·03	97·1
^{51}Cr *B*	$K_2Cr_2O_7$	6 weeks	0·03	96·8
Blank	$K_2Cr_3O_{10}$	0	0·02	—
^{52}Cr *C*	$K_2Cr_3O_{10}$	2 weeks	0·38	69·0
^{51}Cr *C*	$K_2Cr_3O_{10}$	6 weeks	0·88	72·7
Blank	CrO_3	0	0·07	—
^{52}Cr *D*	CrO_3	2 weeks	0·60	79·1
^{51}Cr *D*	CrO_3	6 weeks	1·20	80·8

The methods of measurement of the retention and radiolytic reduction have been described in an earlier paper[1]. The potassium chromate, dichromate, and chromic anhydride used were of analytical reagent quality and were stored before irradiation in a vacuum desiccator over sulphuric acid. Potassium trichromate was prepared from a mixture of potassium dichromate, chromic acid, and water in quantities calculated from the phase diagrams for the formation of potassium trichromate[3] (16·5 g $K_2Cr_2O_7$, 42·5 g CrO_3 in 41 g water). The mixture was heated to 60°C. On cooling to room temperature a large crop of well-developed deep-red crystals separated. The oxidizing equivalent weight of the product was determined by potentiometric titration, 42·85. (Theoretical value, 43·80.) The crystals were purified by recrystallization from nitric acid of sp. gr. 1·22. After one crystallization the equivalent weight became 43·48, and after a second, 43·97. This product was dried in an oven at 110°C for 2 hr and stored in a vacuum desiccator.

[1] Green, G. Harbottle and A. G. Maddock *Trans. Faraday Soc.* **49**, 1413 (1953).
[2] Green and A. G. Maddock *Nature, Lond.* **164**, 788 (1949).
[3] Jäger and Krüss *Ber. dtsch. chem. Ges.* **22**, 2028 (1889).

Several attempts were made to synthesize the reported[4] potassium tetrachromate, but a single solid phase of this composition could not be isolated.

The samples were neither powdered nor sieved to a standard crystal size distribution before use. All samples were sealed *in vacuo* in silicon ampoules for irradiation. All the irradiations were carried out at a nominal pile factor of 3·5, equivalent to a neutron flux of about $3{\cdot}5 \times 10^{11}$ neutrons/cm² sec. The temperature during irradiation in no case exceeded 40°C.

No measurable radiolytic decomposition of the potassium chromate was found, even after 6 weeks irradiation. Indeed, the trivalent chromium content of the material appeared to fall slightly, possibly owing to the decomposition during irradiation of traces of organic reducing reagents fortuitously present. The 6 weeks irradiated dichromate and all the other irradiated samples gave visual evidence of radiolysis by evolving bubbles of oxygen on solution in water. The series chromate, dichromate, trichromate, chromic anhydride become increasingly sensitive to radiation decomposition, substantiating the hypothesis that in a group of chemically similar compounds the sensitivity to radiolysis is related to the inherent density of defects in the average crystals of the different compounds.

There is no obvious relation between the values of the retention and the other properties of the different compounds, nor does it appear that the increase in retention with the time of irradiation is simply related to the amount of radiolytic damage.

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[4] Siewert *Z. Naturw.* **19**, 11 (1862).

The reaction of sodium borohydride with olefinic halides in polyether solution

(*Received* 24 *May* 1957)

We wish to report a reaction which appears to provide a feasible and general method for the preparation of alkyl diboranes, and, possibly, of boron trialkyls, through disproportionation of the substituted diboranes.

When a solution of sodium borohydride (38·2 mmoles) tetraethylene glycol dimethyl ether (15 ml) is allowed to stand for 12 hr in contact with vinyl bromide (35·4 mmoles) at room temperature a white solid is precipitated. Diethyl diborane may be isolated from the reaction mixture along with small quantities of hydrogen and ethane by fractional condensation through traps held at −63°C and −78°C. Diethyl diborane passes through the −63°C trap and is retained in the −78°C trap.

Analysis of the diethyl diborane was carried out by hydrolysis (for active hydrogen) and by oxidation with fuming nitric acid (for boron and carbon). The observed percentages of boron, carbon, and active hydrogen were 25·2, 59·2, and 4·62; the calculated values are 25·2, 57·5, and 4·82. The molecular weight (by vapour density) was found to be 90·0 compared with a calculated value of 83·6. Its vapour pressure at −23·2°C was 10·4 mm compared with a reported value of 10 mm at this temperature.[1]

Since alkyl diboranes are known to take part in complex equilibria involving all of the substituted diboranes as well as boron trialkyls and diborane, no attempt was made to isolate all of the known compounds. Instead the mixture was hydrolysed and the hydrogen evolved (50·9 mmoles) was assumed, for the purpose of calculation, to come from hydrolysis of diethyl diborane, formed according to:

$$NaBH_4 + CH_2{=}CHBr \rightarrow NaBr + 1/2(C_2H_5)_2B_2H_4$$

On this basis, the yield was determined to be 72 per cent, based on vinyl bromide used.

A solution of sodium borohydride (28·0 mmoles) in tetraethyl glycol dimethyl ether (10 ml) reacted rapidly with allyl bromide (23·45 mmoles) even below room temperature.

The reaction mixture was found to contain dipropyl diborane, which was isolated by fractionation through traps held at −30 and −63°C. The dipropyl diborane passed through the −30°C trap

[1] H. I. Schlesinger, L. Horvitz and A. B. Burg *J. Amer. chem. Soc.* **58**, 407 (1936).

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and was retained in the −63°C trap. Its vapour pressure at 0°C was observed to be 3·7 compared with a reported value of 2·8 mm,[1] and it yielded 33·1 mmoles of hydrogen per gramme on hydrolysis, as compared with the calculated value of 32·9 mmoles.

Theoretically, the possibility of forming either *n*-propyl or *iso*propyl diboranes, or both, exists. Hydrolysis of dipropyl diborane yielded a boronic acid with a melting point of 105–107°C. (The reported value for *n*-propyl boronic acid is 107°C.[2] Oxidation of the boronic acid with hydrogen peroxide (followed by treatment with MnO_2 to destroy the excess H_2O_2) yielded a solution which gave a negative iodoform test, indicating the absence of *iso*propyl alcohol. These results make it appear quite probable that the normal propyl group alone is involved.

The yield for this reaction was calculated in the same manner described above, and using the following equation as a basis,

$$NaBH_4 + CH_2{=}CH{-}CH_2Br \rightarrow NaBr + 1/2(CH_2CH_2CH_2)_2B_2H_4$$

was 80 per cent (based on allyl bromide used) for a typical preparation.

Vinyltrichlorosilane failed, in experiments analogous to those described above, to yield similar results. Instead, cleavage of the Si—C bond, producing SiH_4, was observed.

It may be mentioned that BROWN and RAO[3] have reported reactions between sodium borohydride and olefins in the presence of aluminium chloride and diglyme to produce trialkyl boranes.

Acknowledgement—We wish to acknowledge the support of this work by Callery Chemical Company.

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[1] E. KRAUSE and R. NITSCHE *Ber. dtsch. chem. Ges.* **54B**, 2784–91 (1921).
[2] H. C. BROWN and S. V. RAO *J. Amer. chem. Soc.* **78**, 5694 (1956).

Separation of niobium from zirconium by a cation exchanger

(*Received* 11 *June* 1957)

SEVERAL papers have appeared dealing with the separation of zirconium and niobium by an ion exchange method,[1–4] but by all these methods the zirconium is eluted first from the column. However, from the point of view of an investigation of short-lived niobium nuclides, it is very desirable to elute the niobium and retain on the column the zirconium. Such a method was developed here. The high stability of niobium perhydroxy complex suggested that niobium might be desorbed from cation exchange resins with a dilute hydrogen peroxide solution. The formation of zirconium perhydroxy complex is expected to be suppressed by the addition of a mineral acid to the solution.

The process we used consisted essentially of absorption of zirconium (carrier-free ^{95}Zr) and niobium (carrier-free ^{95}Nb) from 0·1 N hydrochloric acid on the top of a column of cation exchanger (Dowex 50W × 8, 200–400 mesh), and continued elution with hydrochloric acid solution containing hydrogen peroxide until the niobium had been removed. Zirconium was then stripped from the column, using 0·5 per cent oxalic acid. In each run we used a 3·5 cm × 0·57 cm² column of hydrogen-form cation exchanger and maintained the flow rates at about 1 cm³/cm² min.

The results are shown in Fig. 1. At first, 1 N hydrochloric acid solution containing 3 per cent hydrogen peroxide was used as a eluting agent for the niobium, and next, 0·1 N hydrochloric acid

[1] E. H. HUFFMAN, G. M. IDDINGS, and R. C. LILLY *J. Amer. chem. Soc.* **73**, 4474 (1951).
[2] K. A. KRAUS and G. E. MOORE *Ibid.* **73**, 9 (1951).
[3] R. E. WALKER and W. H. BALDWIN *U.S.A.E.C. Report ORNL-637* (1950).
[4] K. KIMURA and H. SANO *Radioisotopes* **5**, 18 (1956).

TABLE 1

Eluting agent	Nb-fraction (counts/min)	Zr-fraction (counts/min)	Resin residue (counts/min)*
1 N HCl–3 per cent H_2O_2 for Nb, 0·5 per cent $H_2C_2O_4$ for Zr	7705 ± 65	28,513 ± 90	527 ± 10
0·1 N HCl–0·3 per cent H_2O_2 for Nb, 0·5 per cent $H_2C_2O_4$ for Zr	6123 ± 53†	15,151 ± 87	1649 ± 24

* The activities gave the identical decay curve corresponding to the disintegration which reached transient equilibrium as the fed solution.

† The separation was performed after three weeks from the first run. The ratio of ^{95}Nb to ^{95}Zr obtained here is reasonable for this cooling.

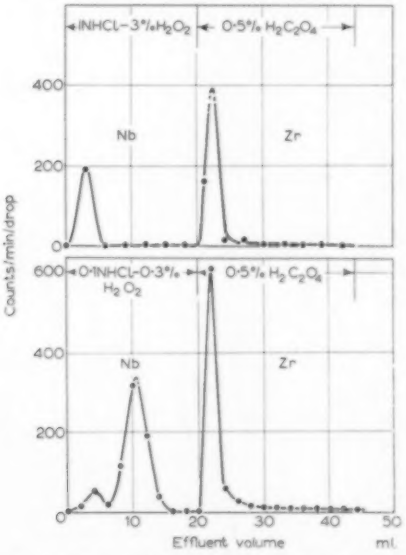

FIG. 1.—Elution of niobium and zirconium from Dowex 50W.

solution containing 0·3 per cent hydrogen peroxide was used. Each fraction eluted was examined with the determination of the β-ray energy absorption curve and the decay curve. Only the niobium fraction eluted with 1 N hydrochloric acid–3 per cent hydrogen peroxide was slightly contaminated with zirconium. In this case, bubbles were formed in the resin bed due to the decomposition of hydrogen peroxide, whereas no bubble was found in the elution with 0·1 N hydrochloric acid–0·3 per cent hydrogen peroxide. The other fractions gave practically pure absorption curves and decay curves corresponding to those of ^{95}Nb and ^{95}Zr. After the elution of zirconium the resins used were decomposed with sulphuric acid and nitric acid. The radioactivity of the residue was determined. The relative radioactivities of the fractions are shown in Table 1, together with their standard deviations.

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PILE NEUTRON ABSORPTION CROSS-SECTION OF ^{83}Kr, ^{131}I and ^{133}Xe

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Abstract—The pile neutron absorption cross-sections of the fission products ^{83}Kr, ^{131}I, and ^{133}Xe have been determined using mass spectrometric techniques. The values were found to be 216 ± 43 barns, 51 ± 40 barns, and 188 ± 89 barns for ^{83}Kr, ^{131}I, and ^{133}Xe respectively.

THE determination of neutron absorption cross-sections is of fundamental importance for both nuclear systematics and reactor technology. Although cross-sections for stable isotopes have been carefully studied, data concerning radioactive isotopes are rather meagre. Several methods are employed to determine neutron absorption cross-sections including the mass spectrometric technique.

LAPP, VAN HORN and DEMPSTER[1] first used mass spectrometric techniques to show that the isotopes ^{149}Sm and ^{155}Gd and ^{157}Gd were responsible for the large neutron absorption of samarium and gadolinium. MACNAMARA and THODE[2] measured the absorption cross-sections for krypton and xenon by the determination of the isotopic ratios before and after neutron irradiation. INGHRAM, HAYDEN and HESS[3] determined cross-sections due to second-order reactions for fission products in the rare-earth region.

The study of cross-sections for radioactive fission products requires measurement of a second-order competing process. As an example consider the following case:

$$\xrightarrow{\beta} D \xrightarrow{\beta} \text{Stable } E$$
$$\uparrow P(c)$$
$$\xrightarrow{\beta} F \xrightarrow{\beta} \text{Stable } G$$
$$P(d)$$

where the nuclide F can undergo decay or capture. The capture probability is

$$P(c) = \frac{\sigma\varphi}{\sigma\varphi + \lambda} = \frac{\sigma\varphi}{\Gamma}$$

and the decay probability

$$P(d) = \frac{\lambda}{\Gamma}$$

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[1] R. E. LAPP, J. R. VAN HORN and A. J. DEMPSTER *Phys. Rev.* **71**, 745 (1947).
[2] J. MACNAMARA and H. G. THODE *Phys. Rev.* **80**, 296 (1950).
[3] M. INGHRAM, R. HAYDEN and D. HESS *Phys. Rev.* **79**, 271 (1950).

where λ is the decay constant for F,
σ is the neutron absorption cross-section for F,
φ is the neutron flux, and
$\Gamma = \sigma\varphi + \lambda$

If the ratio E/G is obtained for two samples having widely different irradiation conditions it is possible to find the value of σ, providing the neutron flux is known. The limit of detection and precision for the measurement of cross-sections depends upon λ, φ and the accuracy to which the ratio E/G can be determined.

EXPERIMENTAL

Two samples of plutonium aluminium alloy were irradiated with thermal neutrons in the N.R.X. (Chalk River) Reactor. Sample A consisted of 8·9 mg of alloy containing 1·9 mg of plutonium and a 1·15 mg cobalt wire to serve as flux monitor. The alloy was approximately spherical in shape with an effective radius of 0·09 cm. This sample was irradiated for a 20 day period in a high flux position where the thermal neutrons were considered to have a Maxwellian distribution of velocities corresponding to a temperature of 100°C. Sample B consisted of 263·0 mg of plutonium aluminium alloy containing 23·9 mg of plutonium. The alloy was approximately hemispherical in shape with a radius of 0·35 cm. This sample was irradiated at a low neutron flux for a 10 day period.

After removal from the reactor, the samples were allowed to decay for a time long compared with the half-life of ^{131}I. The rare gases produced from fission were extracted by melting the alloy in an induction furnace. The released gases were purified with a calcium furnace and then analysed in a 10 in., 90° direction focusing mass spectrometer employing an electron multiplier for the detector. The output from the multiplier was integrated and amplified by means of a vibrating reed electrometer.

The sample of cobalt was dissolved in 0·5 ml of aqua regia and diluted with 50 ml of distilled water. Aliquots were taken and absolute beta counting done using 4π and coincidence techniques.

RESULTS

The flux associated with sample A was monitored with ^{59}Co which had a specific activity of $S = (1{\cdot}79 \pm 0{\cdot}02) \times 10^{11}$ disintegrations sec^{-1} g^{-1} at the time of removal from the reactor. The specific activity is related to the neutron flux by the expression

$$S = {}^{60}_{39}\lambda \, {}^{59}_{39}\sigma\varphi \, \frac{N_0\{\exp(-{}^{59}_{39}\sigma\varphi T) - \exp(-{}^{60}_{39}\lambda T)\}}{{}^{60}_{39}\lambda - {}^{59}_{39}\sigma\varphi} \qquad (1)$$

where ${}^{60}_{39}\lambda$ = the decay constant for ^{60}Co $= 4{\cdot}13 \times 10^{-9}$ sec^{-1},
${}^{59}_{39}\sigma$ = the thermal neutron absorption of ^{59}Co,
$= (37 \pm 1{\cdot}5) \times 10^{-24}$ cm^2,
φ = the thermal neutron flux in the cobalt,
N_0 = the number of atoms in a gram of ^{59}Co,
T = the irradiation time $= 1{\cdot}65 \times 10^6$ sec.

If ${}^{59}_{39}\sigma\varphi T \ll 1$ and ${}^{60}_{39}\lambda T \ll 1$, equation (1) can be reduced to the form,

$$S = {}^{60}_{39}\lambda \, {}^{59}_{39}\sigma\varphi N_0 T \qquad (2)$$

which is applicable to this case. Solving equation (2) gives a value of $(6{\cdot}54 \pm 0{\cdot}25) \times 10^{13}$ neutrons cm^{-2} sec^{-1} for the neutron flux in the cobalt.

To calculate the cross-sections for fission products it is necessary to know the relationship between the flux in the cobalt monitor and the flux in the plutonium aluminium alloy. The flux reduction within the alloy due to self shielding can be evaluated from the calculations of CASE, DE HOFFMANN and PLACZEK.[4] These authors have shown that the ratio of the flux inside an absorbing material located in an isotropic neutron bath to the flux at a large distance outside the material is P_0, the escape probability. Values of $(1 - P_0)$ have been tabulated for spherical objects as a function of the ratio (object radius)/(absorption mean free path).

The absorption mean free path is given by

$$L = 1/N\sigma_{\text{eff}}$$

where L is the absorption mean free path, N the number of plutonium atoms per cm^3, and σ_{eff} the effective neutron absorption cross-section. The neutron absorption cross-section for plutonium does not vary inversely with neutron velocity. If the neutron velocity in the reactor is assumed Maxwellian, then the effective cross-section as given by HUGHES and HARVEY[5] is

$$\sigma_{\text{eff}}(\theta) = \sigma_{\text{abs}}(\theta)f$$

where θ is the neutron temperature, $\sigma_{\text{abs}}(\theta)$ the neutron absorption cross-section for temperature θ, and f is the correction factor for a Maxwellian distribution of velocity and a non "$1/v$" cross-section. For a neutron temperature of 100°C the value of L was found to be 0·493 cm. The ratio of the sample radius to the absorption mean free path is 0·176. The results of CASE *et al.*[4] predict an average flux depression of 11·9 per cent within the sample. The physical dimensions of the cobalt were such as to make any self shielding corrections negligible. Therefore the average flux within the alloy was 0·881 of that found for the cobalt monitor.

Sample B was not monitored and the values listed in Table 1 were obtained from the pile log after self shielding corrections, analogous to those for sample A, had been made. Table 1 summarizes the irradiation conditions for both samples.

TABLE 1.—IRRADIATION CONDITIONS FOR PLUTONIUM SAMPLES

	Irradiation time (hours)	Neutron flux (neutrons cm^{-2} sec^{-1})
Sample A	457·9	$(5{\cdot}76 \pm 0{\cdot}23) \times 10^{13}$
Sample B	240	$(2{\cdot}10 \pm 0{\cdot}10) \times 10^{13}$

The results of the mass spectrometric analysis are given in Table 2. The ratio ^{84}Kr/^{83}Kr is actually the ratio of the fission yields for the 84 and 83 mass chains. The errors quoted are the most probable errors obtained for a large number of spectrograms.

[4] K. M. CASE, F. DE HOFFMANN and G. PLACZEK *Introduction to the Theory of Neutron Diffusion* Vol. 1. U.S. Government Printing Office, Washington, D.C. (1953).

[5] D. J. HUGHES and J. A. HARVEY *Neutron Capture Cross-Sections, Brookhaven National Laboratory Report* BNL-325 (1955).

The neutron absorption cross-section of ^{133}Xe

For a continuous irradiation the amount of neutron capture by ^{133}Xe is given by the expression

$$C = \frac{R\,{}^{133}Y\,{}^{133}_{54}\sigma\varphi}{{}^{133}_{54}\lambda({}^{133}_{54}\lambda - {}^{133}_{53}\lambda)}\left\{({}^{133}_{54}\lambda - {}^{133}_{53}\lambda)T - \frac{{}^{133}_{53}\lambda}{{}^{133}_{54}\lambda}(1 - \exp[-{}^{133}_{54}\lambda T]) - \frac{{}^{133}_{54}\lambda}{{}^{133}_{53}\lambda}(1 - \exp[-{}^{133}_{53}\lambda T])\right\} \quad (3)$$

where $R = {}^{239}_{94}\sigma_f\varphi\,{}^{239}_{94}N$, the number of fissions per second,

^{133}Y = the yield of the 133 mass chain for plutonium fission given by FLEMING and THODE[6] to be $0{\cdot}925\,{}^{134}Y$,

T = the irradiation time.

The fraction of the 133 mass chain which undergoes capture is given by the relation

$$F = C/R\,{}^{133}Y \quad (4)$$

Unfortunately the reactor did not operate continuously throughout the irradiation so that equation (3) had to be evaluated several times to allow for the decay of the

TABLE 2.—RELATIVE YIELDS OF SOME KRYPTON AND XENON ISOTOPES OCCURRING IN THE THERMAL NEUTRON FISSION OF ^{239}Pu

	$^{84}Kr/^{83}Kr$	$^{132}Xe/^{131}Xe$	$^{134}Xe/(^{131}Xe + {}^{132}Xe)$
Sample A	$1{\cdot}631 \pm 0{\cdot}004$	$1{\cdot}395 \pm 0{\cdot}002$	$0{\cdot}8197 \pm 0{\cdot}0013$
Sample B	$1{\cdot}604 \pm 0{\cdot}006$	$1{\cdot}387 \pm 0{\cdot}003$	$0{\cdot}8165 \pm 0{\cdot}0015$

The most probable error has been quoted.

133 chain during the shut-down periods. When this was done, F was found to be $(2{\cdot}23 \pm 0{\cdot}08) \times 10^{19}\,{}^{133}_{54}\sigma$.

The assumption that there is negligible capture in sample B introduces a 1 per cent error which is small compared with the experimental error. The reaction $^{133}Xe(n,\gamma)\,^{134}Xe$ increases the yield of the 134 chain relative to the sum of the 131 and 132 chains. Because of this, the fraction of the 133 chain undergoing capture can be determined from the expression

$$F = \frac{{}^{134}Y_A - {}^{134}Y_B}{{}^{133}Y_B} = \frac{{}^{134}Y_A - {}^{134}Y_B}{0{\cdot}925\,{}^{134}Y_B} = 0{\cdot}0042 \pm 0{\cdot}0020 \quad (5)$$

Equating the results of equations (4) and (5) gives a value for the ^{133}Xe cross-section of ${}^{133}_{54}\sigma = 188 \pm 89$ barns.

The neutron absorption cross-section of ^{131}I

The ^{132}Xe yield in sample A is increased because of the reactions $^{131}Xe(n,\gamma)^{132}Xe$ and $^{131}I(n,\gamma)^{132}I$. MACNAMARA and THODE[2] determined the value of ${}^{131}_{54}\sigma$ to be

[6] W. H. FLEMING and H. G. THODE *Canad. J. Chem.* **34**, 193 (1956).

120 ± 15 barns. Proceeding as for the ^{133}Xe case the following relations can be obtained.

The fractional cross-over due to the ^{131}Xe$(n,\gamma)^{132}$Xe was calculated to be

$$0{\cdot}00148 \pm 0{\cdot}00010$$

and that for the ^{131}I$(n,\gamma)^{132}$I case to be

$$3{\cdot}53 \times 10^{19}\ {}^{131}_{53}\sigma.$$

The observed cross-over is

$$F = \frac{{}^{132}Y_A - {}^{132}Y_B}{{}^{131}Y_B} = 0{\cdot}0033 \pm 0{\cdot}0014$$

The observed cross-over due to the reaction ^{131}I$(n,\gamma)^{132}$I is

$$0{\cdot}0018 \pm 0{\cdot}0014$$

Equating this to the calculated ^{131}I$(n,\gamma)^{132}$I cross-over gives a value for the ^{131}I cross-section of

$${}^{131}_{53}\sigma = 51 \pm 40 \text{ barns.}$$

The neutron absorption cross-section of ^{83}Kr

The precursors of ^{83}Kr are short-lived, so that fissions leading to mass 83 appear as ^{83}Kr within a time short compared with the irradiation time. Under such conditions the fractional cross-over to the 84 chain is

$$F = \frac{1 - (1 - \exp[-{}^{83}_{36}\sigma\varphi T])}{{}^{83}_{36}\sigma\varphi T} \tag{6}$$

If ${}^{83}_{36}\sigma\varphi T \ll 1$, equation (6) reduces to the simple expression

$$F = \tfrac{1}{2}\,{}^{83}_{36}\sigma\varphi T$$

Equating the observed and calculated cross-over yields a value for the ^{83}Kr cross-section of

$${}^{83}_{36}\sigma = 216 \pm 43 \text{ barns}$$

DISCUSSION

The cross-sections determined represent the value for 2200 m/sec neutrons provided they are inversely proportional to the neutron velocity. If the cross-section does not vary as $1/v$ the determined value is for neutrons with a Maxwellian distribution corresponding to a temperature of 100°C relative to the cross-section of ^{59}Co at 100°C.

The cross-section of 216 ± 43 barns for ^{83}Kr is in good agreement with the value 205 ± 10 barns obtained by MACNAMARA and THODE.[2] This agreement indicates that the method and assumptions presented here are valid, since the value obtained by these authors was determined by the use of a different technique.

The value for the neutron absorption cross-section of ^{131}I cited by HUGHES and HARVEY[7] is 600 ± 300 barns. This is in complete disagreement with the cross-section of 51 ± 40 barns reported in this paper. Consideration of the cross-sections

[7] D. J. HUGHES and J. A. HARVEY *Neutron Capture Cross-Sections, Brookhaven National Laboratory Report* BNL-325 (1955), unpublished Chalk River value.

in this mass region, particularly for the other isotopes of iodine, suggest the value of 600 barns to be extremely large.

GLENDENIN and STEINBERG[8] have reported an upper limit of 3000 barns for the cross-section of ^{133}Xe. Since this represents only an upper limit, it is in reasonable agreement with the value of 188 ± 89 barns found in this work.

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[8] E. P. STEINBERG and L. GLENDENIN *International Conference on the Peaceful Uses of Atomic Energy, Geneva*, Paper 614 (1955).

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THE CROSS-SECTION OF THE REACTION $^{134}Cs(n\gamma)^{135}Cs$ AND THE HALF-LIFE OF ^{134}Cs

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Abstract—The isotopic composition of caesium samples which had been subject to intense reactor neutron irradiation was measured with a 6 in. radius, 60° sector field, mass spectrometer fitted with a triple filament thermal ionization source. The cross-section of the reaction $^{134}Cs(n\gamma)^{135}Cs$ was calculated from the observed isotopic composition and found to be 134 ± 12 barns. By measuring the change with time of the $^{134}Cs/(^{133}Cs + ^{135}Cs)$ ratio using the mass spectrometer the half life of ^{134}Cs was found to be $2{\cdot}15 \pm \frac{0{\cdot}08}{0{\cdot}04}$ years. In a subsidiary experiment the cross-section of the reaction $^{133}Cs(n\gamma)^{134}Cs$ was found by activation to be $30{\cdot}4 \pm 1{\cdot}7$ barns.

WHEN natural caesium, ^{133}Cs, is subjected to intense neutron bombardment in a reactor the isotopes produced are ^{134}Cs (2·19 years), ^{135}Cs ($2{\cdot}0 \times 10^6$ years), and ^{136}Cs (13 days). The short half-life of ^{136}Cs is unfavourable for the build-up of ^{137}Cs (30 years) and with the highest neutron flux available to us, approximately 5×10^{14} $n/cm^2/sec$, we were not able to detect ^{137}Cs in our mass spectrographic analysis of the irradiated caesium. Since the analyses were carried out several months after the end of bombardment the ^{136}Cs had decayed and of the caesium isotopes only those of masses 133, 134, and 135 were present.

The quantities which determine the isotopic composition of such irradiated caesium are the following:

(a) The neutron flux and the times of the irradiation and decay periods.

(b) The $(n\gamma)$ cross-sections of ^{133}Cs, ^{134}Cs, and ^{135}Cs. It is unlikely that any reactions other than $(n\gamma)$ cause significant changes in the isotopic composition.

(c) The half-life of radioactive decay of ^{134}Cs.

At the beginning of our experiments the following pertinent data were available:

(a) The absorption cross-section of ^{133}Cs for 2200 m/sec neutrons, $29{\cdot}0 \pm 1{\cdot}5$ barns.[1] Neutron absorption should lead almost entirely to the 2·19 years ^{134}Cs, a view which is supported by the (less accurate) value for the activation cross-section of ^{133}Cs to ^{134}Cs, 26 ± 5 barns.[1]

(b) The activation cross-section of ^{135}Cs to ^{136}Cs, very approximately, 15 ± 8 barns.[1]

(c) The half-life of ^{134}Cs, approximately, $2{\cdot}3 \pm 0{\cdot}3$ years.[2]

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[1] D. J. HUGHES and J. A. HARVEY BNL-325 (1955); H. POMERANCE *Phys. Rev.* **83**, 641 (1951).
[2] L. E. GLENDENIN N.N.E.S. Vol. IV, 9, *The Fission Products* p. 1931. McGraw-Hill, New York (1951).

The isotopic composition produced is insensitive to the value of the $^{135}Cs(n\gamma)^{136}Cs$ cross-section and we found that the approximate value was satisfactory for our calculations. Thus, a change by a factor of two in either direction from the quoted value of 15 barns produces a change in the isotopic composition which is less than the error of the mass spectrographic analysis.

Our experiments therefore comprised the following three stages:

(1) Determination of the half-life of ^{134}Cs by measuring mass spectrographically the change with time of the ratio $^{134}Cs/(^{133}Cs + ^{135}Cs)$.

(2) Determination of the effective cross-section for the reaction $^{133}Cs(n\gamma)^{134}Cs$ by an activation method involving short irradiations and making use of the ^{134}Cs half-life determined in (1).

(3) Determination of the cross-section for the reaction $^{134}Cs(n\gamma)^{135}Cs$ from the isotopic composition of long irradiated caesium making use of the data from the literature.[1,2]

While our measurements were in progress three values for the ^{134}Cs half-life became available. These were, first, a measurement of the decay using an ionization chamber and giving a value of 2·06 years,[3] secondly, an electroscope measurement giving 2·09 years,[4] and thirdly a 4π proportional β-counter measurement giving 2·19 years.[5] Of these the last is probably the most accurate since the period over which the decay was followed was greatest (5 years) and since this value is further supported by our own results (2·15 years) we have used it throughout.

EXPERIMENTAL

Neutron irradiations

Two long irradiations were carried out. The first was of approximately 10 mg of spectroscopically pure Cs_2CO_3 in the M.T.R., Idaho, for 140 days. The second was of approximately 10 mg of $CsNO_3$ in the NRX reactor, Chalk River, for 356 days. Two short irradiations were made, each of 16 hr. using a position in NRX similar to that used for the long irradiation. For these irradiations the caesium compounds which were of spectroscopic purity, were dried at 110° C and weighed into silica tubes which were then sealed. CsCl, 36·8 mg, was used in the first irradiation and Cs_2CO_3, 32·1 mg, in the second.

Mass spectrometer measurements

The irradiated material was dissolved in high purity distilled water which had been tested to show that aliquots gave no detectable caesium in the mass spectrometer. Two solutions were prepared from each sample, one of 10 μg Cs^+/ml and the other of 100 μg Cs^+/ml. Both were made slightly acid with sulphuric acid. In all cases the analyses of the "strong" and "dilute" solutions were identical, confirming that the water used did not contain caesium (^{133}Cs).

The mass spectrometer had a 6 in. radius, 60° sector field and triple filament thermal ionization source. The following precautions were taken to eliminate "memory" effects. Before each analysis the source assembly was removed, cleaned and fitted with new filaments. The spectrometer was then operated with a much higher filament temperature than used in the analyses and no traces of caesium were detected. Analyses were then made on the two solutions of different Cs^+ concentration and found to agree in all cases.

The radioactive decay of the caesium isotopes ^{134}Cs and ^{136}Cs produces isobaric barium isotopes. Barium was not separated chemically prior to analysis and thus it was necessary to show that the barium isotopes did not contribute to the caesium peaks. This was done by (a) showing that barium

[3] E. E. LOCKETT Private communication.
[4] G. C. CAMPBELL Private communication.
[5] W. F. MERRITT, P. J. CAMPION and R. C. HAWKINGS *Canad. J. Phys.* **35**, 16 (1957).

compounds on the filament gave no detectable peaks at the filament temperature used for caesium analysis and (b) showing that the addition of barium compounds to caesium compounds introduced no peaks attributable to barium when the mixture was analysed for caesium.

The M.T.R. sample was first analysed 64 days after the end of irradiation and then at intervals of about a month to observe the decay of the ^{134}Cs. During the course of these measurements, which lasted for 1 year, no change in the $^{135}Cs/^{133}Cs$ ratio occurred, showing that there had been no contamination with natural caesium, ^{133}Cs. The NRX sample was analysed 165 days after the end of irradiation.

Activation measurements

(a) *Neutron flux monitors.* These consisted of cobalt wires of certain standard dimensions and weight, viz: diameter 0·013 cm, length 1·0 cm, weight 1·14 $\pm$ 0·005 mg. The monitors were irradiated in the same capsule as the caesium samples and then, after a decay period of 5 days, the ^{60}Co activity was measured in an ionization chamber. This chamber had previously been calibrated for the standard cobalt wires by making measurements on wires which were subsequently dissolved and their ^{60}Co content determined by absolute β-counting in a 4π proportional counter. Changes in the sensitivity of the ion chamber are eliminated by adjusting the instrument to give a standard reading for standard radium sources. The precision of the chamber measurements is $\pm$0·1 per cent. The accuracy with which the ^{60}Co content of the wires can be determined is $\pm$1·5 per cent, the chief source of error being in the absolute β-counting.*

(b) ^{134}Cs *activity.* The samples were allowed to decay for 2 days, when the silica tubes were broken under water and the contents dissolved with addition of a few drops of concentrated sulphuric acid. The solutions were evaporated almost to dryness under a heat lamp and the residues dissolved in water and made up to 2·000 l. Aliquots for β-counting were taken with a calibrated 20 μl pipette.

The β-counter was of conventional 4π design, using methane as counting gas. The sources were mounted on films of VYNS plastic, 10 $\mu g/cm^2$ coated on both sides with gold, 10 $\mu g/cm^2$. A correction of 1·3 per cent was added to the counting rate to allow for absorption by the mounting film.[6] No correction was made for absorption in the source itself. The source weights were in the order of 0·2 μg and the self absorption should not be greater than 2 per cent.

RESULTS AND DISCUSSION

The half-life of ^{134}Cs

The decay of ^{134}Cs is shown by the data of Table 1. The errors shown for the ^{134}Cs percentages are based on the standard deviations between spectrograms. The half-life of ^{134}Cs obtained from these data is $2{\cdot}15 \pm \frac{0{\cdot}08}{0{\cdot}04}$ years. The value obtained by MERRITT *et al.*[5] using a 4π proportional β-counter over a period of 5 years is 2·19 $\pm$ 0·02 years. This latter value was used in our calculations because owing to the longer period over which decay was studied it should be more accurate. Our value of 2·15 years is a useful confirmation of MERRITT's result since the mass spectrometer value is not affected by the problem of radiochemical purity.

The $(n\gamma)$ *cross-section of* ^{133}Cs

The neutron flux for each of the two short irradiations was calculated from the measured ^{60}Co activity using 37·0 barns for the $^{59}Co(n\gamma)^{60}Co$ cross-section and 5·28 years for the half-life of ^{60}Co. This cross-section is that given for the absorption cross-section of ^{59}Co for 2200 m/sec neutrons[1] and the half-life is that used in the same reference. The fluxes so calculated were reduced by 2 per cent which is the approximate epicadmium contribution for cobalt in the reactor position used.[7]

* This system of flux monitoring has been developed by the co-operation of several groups of workers at Chalk River and is now used fairly extensively throughout the Chalk River Project. A report is being prepared.

[6] B. D. PATE and L. YAFFE *Canad. J. Chem.* **33**, 929 (1955).

[7] R. E. JERVIS Private communication.

Table 1. Decay of ^{134}Cs

Time from first analysis (days)	Percentage $^{134}Cs = \frac{100 \times {}^{134}Cs}{{}^{134}Cs + {}^{133}Cs + {}^{135}Cs}$	$100 \times {}^{134}Cs/1\text{-}{}^{134}Cs = \frac{100 \times {}^{134}Cs}{{}^{133}Cs + {}^{135}Cs}$
0	5·679 ± 0·08	6·021
29	5·586 ± 0·04	5·917
32	5·577 ± 0·04	5·906
66	5·429 ± 0·03	5·741
104	5·305 ± 0·05	5·602
140	5·160 ± 0·05	5·441
153	5·041 ± 0·04	5·309
197	4·869 ± 0·04	5·118
301	4·436 ± 0·04	4·642
351	4·287 ± 0·04	4·479

This gives the thermal flux defined as the flux value which when multiplied by the 2200 m/sec cross-section of a "$1/v$" detector gives the rate of reaction between the detector and the sub-cadmium neutrons.

The ^{133}Cs cross-section in each irradiation was calculated from the corrected ^{134}Cs activity using 2·19 years for the half-life of ^{134}Cs and the flux value as defined above. For the CsCl irradiation the result was 31·2 ± 0·7 barns and for the Cs_2CO_3 irradiation 29·6 ± 0·7 barns. The errors quoted are the non-systematic ones of which the fluctuation between sources, standard deviation ±2 per cent, is the most important. In addition to these errors there are systematic ones of which the most important are: the absolute disintegration rate of the ^{134}Cs ± 2 per cent, the calibration of the flux monitoring system ±1·5 per cent and the $(n\gamma)$ cross-section of ^{59}Co ± 4 per cent. We estimate the overall error as 5·5 per cent and quote the result for the $^{133}Cs(n\gamma)^{134}Cs$ cross-section as 30·4 ± 1·7 barns. This result does not differ significantly from the absorption cross-section of ^{133}Cs for 2200 m/sec neutrons, 29·0 ± 1·5 barns, and we have used the latter (probably more reliable) value in our calculations of the ^{134}Cs cross-section, below.

The $(n\gamma)$ cross-section of ^{134}Cs

The composition of the long-irradiated samples were as follows: M.T.R. sample 98 days after end of irradiation, ^{133}Cs 93·19 per cent, ^{134}Cs 5·577 ± 0·04 per cent, ^{135}Cs 1·232 ± 0·02 per cent; NRX sample 165 days after irradiation, ^{133}Cs 96·26 per cent, ^{134}Cs 3·25 ± 0·02 per cent, ^{135}Cs 0·49 ± 0·01 per cent. In each case the cycle of reactor "on" and "off" periods was complex; in addition the M.T.R. sample was irradiated in several positions of considerably different flux. Under these circumstances the computation of the expected isotopic composition is laborious and we were fortunate in having an analogue computer.

Each experiment yields a ratio ^{133}Cs : ^{134}Cs : ^{135}Cs which contains two independent pieces of information. Thus, out of the parameters which determine the isotopic composition two may be treated as unknowns and their values obtained. In the present case the unknowns were the neutron flux and the cross-section for the reaction

$^{134}Cs(n\gamma)^{135}Cs$. The procedure used was as follows. The neutron flux was estimated from reactor operation records and using this preliminary flux value the computer was used to calculate the isotopic compositions which would have resulted for various chosen values of the ^{134}Cs cross-section. Curves could then be constructed showing how the $^{134}Cs/^{133}Cs$ and $^{135}Cs/^{134}Cs$ ratios varied with ^{134}Cs cross-section (at the particular flux level used). It was then apparent that no value of the cross-section existed which gave the correct (observed) answer for both ratios. The calculations were then repeated using different flux values and families of curves constructed. From these it was possible to find the unique combination of flux and cross-section which corresponded to the observed ratios. The effect of changing the values of the other parameters, i.e. the ^{134}Cs half-life and the ^{135}Cs cross-section was found by making representative calculations to show how the families of curves were displaced by changing these other parameters. To find the error in the ^{134}Cs cross-section permitted by the experimental errors the families of curves were examined to find how much the ^{134}Cs cross-section could be changed and, given the most favourable flux, still lead to values of the ratios which were within the experimental limits. The value for this cross-section obtained from the M.T.R. data is 131 $\pm$ 7 barns, and from the NRX data 139 $\pm$ 14 barns. The errors include those arising from the experimental errors in the isotopic composition, from the uncertainty in the ^{134}Cs half-life and from the uncertainty in the $^{135}Cs(n\gamma)^{136}Cs$ cross-section, but not that from the uncertainty in the $^{133}Cs(n\gamma)^{134}Cs$ cross-section which introduces a further error of $\pm$7 barns. If the M.T.R. result is given twice the weight of the NRX result and the errors are treated as though they were statistical the value obtained for the $^{134}Cs(n\gamma)^{135}Cs$ cross-section is 134 $\pm$ 12 barns. This is an effective value based on the relative rates of the reactions $^{134}Cs(n\gamma)^{135}Cs$ and $^{133}Cs(n\gamma)^{134}Cs$ and taking the cross-section of the latter reaction as 29·0 barns; a value of 140 barns would be obtained with our figure of 30·4 barns for the latter reaction.

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A SCALE OF ELECTRONEGATIVITY BASED ON ELECTROSTATIC FORCE

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Abstract—An equation is presented for the evaluation of electronegativity from the force of attraction between a nucleus and an electron from a bonded atom. From this simple electrostatic approach, the electronegativities of forty-four elements are calculated. The results are compared with certain previously proposed scales of electronegativity.

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ELECTRONEGATIVITY was first defined by PAULING[1] as "the power of an atom in a molecule to attract electrons to itself." PAULING found an empirical relation between the *energy* of a bond and the electronegativities of the bonded atoms and, from this relation, estimated the electronegativities of several elements. Other electronegativity scales based on such diverse physical properties as stretching force constants, dipole moments, ionization potentials, and electron affinities have been proposed and are discussed in a recent review.[2] In the construction of each scale of electronegativity, some property dependent upon electron distribution, not electron distribution itself, was measured. Since the effects of the electronegativity of an atom in a molecule are more or less obscured by other contributing factors, the accurate quantitative evaluation of electronegativity is exceedingly difficult from both theoretical and experimental standpoints. However, the concept of electronegativity and the existing scales have enabled the correlation and explanation of a vast number of observations.

The purpose of the present paper is to introduce a scale of electronegativity based on the force of attraction between the nucleus and an electron from a bonded atom. To circumvent formidable calculations, the attractive force will be estimated from the simple rules of electrostatics involving point charges. If r is the distance between an electron and a nucleus, e is the charge on the electron, and eZ_{eff} is the charge which is effective at the electron due to the nucleus and its surrounding electrons, the force of attraction is given by

$$\text{Force} = \frac{e^2 Z_{eff}}{r^2} \qquad \text{(A)}$$

The electron is considered to be at the covalent boundary, r, of the atom. The effective nuclear charge is less than the actual nuclear charge due to screening by the electrons in the atom. The force of attraction given by equation (A) is proposed as an approximate measure of the extent to which an atom in a molecule attracts

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[1] L. PAULING *The Nature of the Chemical Bond* Chap 2. Cornell University Press, Ithaca, New York (1939).

[2] H. O. PRITCHARD and H. A. SKINNER *Chem. Rev.* **55**, 745 (1955).

electrons to itself, and therefore a measure of what might be called the absolute electronegativity of the atom.

The quantity Z_{eff}/r^2, for thirty-one elements (for which PAULING has assigned electronegativity values) was calculated, using covalent radii exclusively from his work[3]* and SLATER's rules[4] for determining the effective nuclear charge. The results are recorded in Table 1 and plotted in Fig. 1 against PAULING's electronegativity

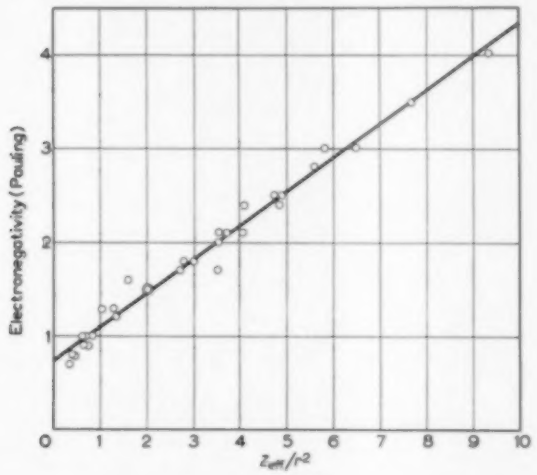

FIG. 1.

values.[2] The best straight line in Fig. 1 was obtained by the method of least-squares. In view of the inaccuracies in r, in Z_{eff}, and possibly in PAULING's electronegativity values, the proximity of the points to the line is noteworthy.

The magnitudes of Z_{eff}/r^2 represent "absolute" electronegativities, and differ from PAULING's relative values. The two scales can be made to coincide by expressing the electronegativity, χ, from this electrostatic approach as a linear function of Z_{eff}/r^2, taking the appropriate constants from Fig. 1:

$$\chi = 0{\cdot}359\,\frac{Z_{eff}}{r^2} + 0{\cdot}744 \qquad \text{(B)}$$

The electronegativity values calculated from equation (B) for forty-four elements are listed in column 4 of Table 1.

Since the ability of an atom in a molecule to attract electrons depends upon the combination of orbitals used for bonding, and since most elements exhibit more than one type of hybridization in their compounds, it is more accurate to speak of orbital electronegativity and to assign a range of electronegativity values to an element than to consider electronegativity as an invariant atomic property. For example, the electronegativity of carbon in the carbon–hydrogen bond is well known to depend upon the hybridization of carbon. In the series, ethane–ethene–ethyne, carbon

* The radius depends upon the hybridization of bonding orbitals, of course, and more will be said of this later.

[3] L. PAULING *J. Amer. chem. Soc.* **69**, 542 (1947).
[4] J. C. SLATER *Phys. Rev.* **36**, 57 (1930).
[5] W. GORDY *Phys. Rev.* **69**, 604 (1946).

TABLE 1.—ELECTRONEGATIVITY VALUES FROM ELECTROSTATICS

	Z_{eff}	$\frac{Z_{eff}}{r^2}$	$0{\cdot}359\frac{Z_{eff}}{r^2}+0{\cdot}744$	PAULING'S[1] thermal data	GORDY[5] χ_s	PRITCHARD and SKINNER[2]
Li	0·95	0·633	0·97	1·0	0·96	0·965
Na	1·85	0·749	1·01	0·9	0·90	0·91
K	1·85	0·451	0·91	0·8	0·82	—
Rb	1·85	0·397	0·89	0·8	0·79	—
Cs	1·85	0·335	0·86	0·7	0·78	—
Be	1·60	2·024	1·47	1·5	1·38	1·43
Mg	2·50	1·344	1·23	1·2	1·16	1·19
Ca	2·50	0·829	1·04	1·0	1·03	—
Sr	2·50	0·682	0·99	1·0	0·98	—
Ba	2·50	0·637	0·97	0·9	0·93	—
Sc	2·65	1·280	1·20	1·30	1·27	—
Y	2·65	1·015	1·11	1·30	1·21	—
La	2·65	0·928	1·08	—	1·17	—
Ti	2·80	1·597	1·32	1·6	1·57	—
V	2·95	1·969	1·45	—	1·93	—
Cr	3·10	2·267	1·56	—	2·24	—
Mn	3·25	2·382	1·60	—	2·60	—
Fe	3·40	2·505	1·64	—	—	—
Co	3·55	2·652	1·70	—	—	—
Ni	3·70	2·802	1·75	—	—	—
Cu	3·85	2·798	1·75	—	0·96	1·07
Ag	3·35	1·868	1·42	—	0·91	1·11
Zn	4·00	2·564	1·66	—	1·21	1·32
Cd	4·00	2·003	1·46	—	1·13	1·23
B	2·25	3·516	2·01	2·0	1·91	2·00
Al	3·15	2·022	1·47	1·5	1·48	1·50
Ga	4·65	3·000	1·82	—	1·48	1·60
In	4·65	2·075	1·49	—	1·36	1·48
C	2·90	4·878	2·50	2·5	2·52	2·51
Si	3·80	2·762	1·74	1·8	1·82	1·84
Ge	5·30	3·543	2·02	1·7	1·77	1·87
Sn	5·30	2·708	1·72	1·7	1·61	1·74
N	3·55	6·483	3·07	3·0	3·01	3·02
P	4·45	3·678	2·06	2·1	2·19	2·20
As	5·95	4·064	2·20	2·0	2·04	2·12
Sb	5·95	2·993	1·82	1·8	1·82	1·93
O	4·20	7·670	3·50	3·5	3·47	3·48
S	5·10	4·715	2·44	2·5	2·58	2·58
Se	6·60	4·821	2·48	2·4	2·35	2·42
Te	6·60	3·517	2·01	2·1	2·08	2·21
F	4·86	9·356	4·10	4·0	3·94	4·00
Cl	5·75	5·820	2·83	3·0	3·00	2·98
Br	7·25	5·559	2·74	2·8	2·68	2·73
I	7·25	4·074	2·21	2·4	2·36	2·50

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becomes more electronegative with increasing *s*-character in the carbon-hydrogen bond. This trend is predicted by the electrostatic force scale of electronegativity, for the covalent radius decreases with increasing *s*-character, and the nuclear charge effective at the hydrogen electron increases due to less shielding by the carbon electrons. The electronegativity values listed in column 4 of Table 1 are based on the most common covalent radii.

Prior to this research, GORDY defined electronegativity "for a neutral atom in a stable molecule as the potential at a distance r (covalent radius) from its nucleus which is caused by the nuclear charge effective at that distance."[5] The effective nuclear charge was estimated with the assumptions that electrons in closed shells exert full screening power and that the screening constant of one valence electron for another is 0·5. Thus the *potential* at the covalent boundary is considered to be a measure of the absolute electronegativity and is given by

$$\chi_1 = \frac{e[n - 0{\cdot}5(n-1)]}{r} = \frac{0{\cdot}5e(n+1)}{r} \qquad \text{(C)}$$

To enable a comparison of electronegativity values predicted by this method with previously proposed values, the constants in equation (C) were changed such that the electronegativity values, χ_2, fall into the same range as Pauling's values:

$$\chi_2 = 0{\cdot}31\,\frac{(n+1)}{r} + 0{\cdot}50 \qquad \text{(D)}$$

The electronegativity values calculated from equation (D) agree well with Pauling's values as shown by Table 1. It is noted that the values for r were selected from several sources. PRITCHARD and SKINNER reviewed[2] the relation between atomic electrostatic surface potential and electronegativity, objected to GORDY's simplification with respect to effective nuclear charge, and computed an electronegativity scale using SLATER's more widely accepted method[4] for determining Z_{eff}. However, it was necessary to fit different constants in equation (D) for each row of the periodic table. PRITCHARD and SKINNER[2] appear to have calculated the potential caused by the nucleus acting on the ultimate electron and corrected for the screening caused by the other electrons. Their values are recorded in column 7 of Table 1.

Column 3 of Table 1 indicates that in Group III-B–VI-B the electronegativities of the elements in the Fourth Period are greater than the electronegativities of the corresponding elements in the Third Period. For example, the electronegativities of silicon and germanium are 1·74 and 2·02, respectively. This order is neither consistent with the electronegativity values that were originally assigned[1] nor with the customary interpretation of the periodic table. However, the authors have compiled extensive evidence (to be published in this journal) that the electronegativity of germanium is indeed greater than that of silicon. It may be noted here that the point farthest below the line in Fig. 1 corresponds to germanium. SANDERSON[6,7] has proposed a scale of electronegativity based on the "stability ratio" which also shows an alternation with period number. SANDERSON lists[8] a large number of observations which are consistent with his scale of alternating electronegativity and which otherwise

[6] R. T. SANDERSON *J. chem. Educ.* **29**, 539 (1952).
[7] R. T. SANDERSON *J. chem. Phys.* **23**, 2467 (1955).
[8] R. T. SANDERSON *J. Amer. chem. Soc.* **74**, 4792 (1952).

would be chemical anomalies. The scales based on "stability ratio" and electrostatic force are in general agreement, and the calculations involving Z_{eff}/r^2 indicate that it may be possible to explain the alternation in electronegativity going down the groups near the centre of the periodic table in terms of relative electron packing in the different periods. As the atomic number in a given period increases, the magnitude of the radius increases montonically but not regularly, since the numbers of electrons added are 8, 8, 18, 18, and 32.

The relative electronegativities of the elements in the first transition series are comparable to the relative stabilities of their co-ordination compounds. Several investigations[9–12] have shown the existence of a "natural order of stability," $Mn < Fe < Co < Ni < Cu > Zn$, regardless of the nature of the co-ordinated ligand. The electronegativity values from equation (B) are: $Mn\ (1{\cdot}60) < Fe\ (1{\cdot}64) < Co\ (1{\cdot}70) < Ni\ (1{\cdot}75) = Cu\ (1{\cdot}75) > Zn\ (1{\cdot}66)$. This correlation is expected, since the strength of the metal-ligand hand should be a function of the electron-attracting tendency of the metal.

The use of electrostatic force to evaluate electronegativity is fully consistent with Pauling's original definition. Electrostatic force measures the tendency to attract (say bonded) electrons, whereas electrostatic potential measures the work necessary for complete separation of the charges. It is noted that Mulliken's scale of electronegativity, based on the average of the electron affinity and ionization potentials of atoms,[13] is a measure of potentials or work and, therefore, is not expected to parallel the electrostatic force scale. The above-mentioned chemical anomalies are explained by the electrostatic force scale of electronegativity, but not by the electrostatic potential scale.

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ELECTRONEGATIVITIES OF CARBON, SILICON, GERMANIUM, TIN AND LEAD

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Abstract—The chemical reactions of analogous compounds of carbon, silicon, germanium, tin and lead are discussed briefly and shown to be inconsistent with the customary interpretation of the Mendeléeff periodic table and with the most widely accepted values of electronegativity. The electronegativities of these elements are calculated herein from data supplied by nuclear quadrupole resonance, by work functions, by calculations based on thermochemical data and by calculations based on electrostatics. In addition, relative electronegativities for these elements are determined experimentally by measuring the chemical shift of the tetramethyl derivatives at infinite dilution in carbon tetrachloride as a solvent. The electronegativity values 2·60 for carbon, 1·90 for silicon, 2·00 for germanium, 1·93 for tin, and 2·45 for lead are proposed as the most accurate ones applicable to the Group IV–B elements in sp^3 valence states.

PAULING defined electronegativity as "the power of an atom in a molecule to attract electrons to itself."[1] That the electronegativity of an atom depends upon its environment is implied by the following more formal definition: If the bond between atoms A and B can be considered to be an admixture of three extreme structures (the ionic structures A^+B^- and A^-B^+, and the covalent structure A–B), the wave function representing the bond may be expressed as

$$\psi = v_1\psi(A^+B^-) + v_2\psi(A\text{–}B) + v_3\psi(AB)$$

where v_1, v_2, and v_3 are mixing coefficients. If v_1 is larger than v_3, a negative charge resides on B, and B is said to be more electronegative than A. Or more precisely, if ϕ_A and ϕ_B are the particular bonding orbitals, usually hybrids of atoms A and B, and if v_1 is greater than v_3, then ϕ_B is said to be a more electronegative bonding orbital than ϕ_A.

The concept of orbital electronegativity is more accurate than the concept that electronegativity is an invariant atomic property, since an atom may form bonds in different compounds by using different orbitals, in some of which electrons will be held more strongly than in others. As an example, the electron-withdrawing ability (electronegativity) of the carbon-bonding orbital in the *s–p* hybrid carbon–hydrogen bond increases as the percentage of *s* character in that bond in the series ethane, ethene, and ethyne increases. Therefore, it is appropriate to assign to a given element a range of electronegativity values, instead of a single value, depending upon the available valence states. According to this concept of orbital electronegativity, the designation of an electronegativity value for an element is complete if, and only if, the valence state is specified.[2] Hence the establishment of an exact scale of

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[1] L. PAULING *The Nature of the Chemical Bond* Chap. 2. Cornell University Press, Ithaca, New York (1939).

[2] H. O. PRITCHARD and H. A. SKINNER *Chem. Rev.* **55**, 745 (1955).

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electronegativity is exceedingly difficult, from both experimental and theoretical viewpoints, and may not be achieved until the distribution of electrons in molecules can precisely be ascertained. Fortunately, there are several physical properties of which the magnitudes depend to some extent on electronegativity, and these properties have been used indirectly to establish scales of electronegativity. However, the exact dependence of each observable property on electronegativity is not known, and various assumptions are necessary. Fortunately, a close agreement of electronegativity values obtained from measurements of several diverse properties lends confidence and utility to the concept. In this research, the chemical shift of nuclear magnetic resonance, together with nuclear quadrupole coupling constants, bond energies, work functions, and electrostatic calculations, will be employed in the assignment of electronegativity values to the Group IV–B elements.

This research was prompted by chemical observations (discussed in the next section) which were inconsistent with the relative electronegativities that had previously been assigned to silicon, germanium, and tin. PAULING's scale of electronegativity and the customary interpretation of Mendeléeff's periodic table led to the generalization that within any given group, electronegativity decreases with increasing atomic number. According to this generalization, the electronegativity of the Group IV–B elements should decrease in the order carbon > silicon > germanium > tin > lead. However, in some of its reactions germanium appeared to be more electronegative than either silicon or tin in the reactions of their analogous compounds. Also, chemical evidence compiled by SANDERSON led to a drastically different scale of electronegativity[3,4,5] in which the values for the representative elements in the fourth period of Mendeléeff's periodic table exceed those of the elements in the third and fifth periods. The purpose of the present research was to reinvestigate by every possible precise means the electronegativities of the Group IV–B elements.

The exact valence state (state of hybridization) of a Group IV–B element in its compounds often is not known. For example, in tetravalent compounds, the effects of *d*-orbital bonds and of distortions from tetrahedral symmetry are difficult to determine quantitatively. To eliminate the necessity of specifying the exact valence states in addition to the numerical values of electronegativity, it seemed advisable to investigate relative electronegativities in analogous series of compounds in which each Group IV–B element is bonded with approximately the same admixture of orbitals. It is conceded that the results are applicable in the strictest sense only within the area of compounds chosen for the investigation.

SOME OBSERVATIONS OF COMPOUNDS OF THE GROUP IV-B ELEMENTS

In terms of the general trends in the Mendeléeff periodic system, several analogous series of compounds of the Group IV–B elements exhibit an apparently anomalous chemical behaviour. As the following examples will indicate, germanium (in the fourth period) seems to be more electronegative than silicon (in the third period), and tin (in the fifth period) appears no more electropositive than silicon.

[3] R. T. SANDERSON *J. Amer. chem. Soc.* **74,** 4792 (1952).
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1. Reduction of organogermanium halides with zinc and hydrochloric acid

The reaction of carbon-halogen compounds with zinc and aqueous hydrochloric acid to form carbon–hydrogen compounds is well known. Recently, WEST[6] treated halides of silicon, germanium, and tin with amalgamated zinc and hydrochloric acid, and obtained metal–hydrogen bonds only in the case of germanium. This apparently anomalous reaction of germanium halides indicates that germanium is a more electronegative element than either silicon or tin. Many organoarsenic halides have been reduced to the corresponding hydrides by zinc and aqueous hydrochloric acid. It is noteworthy that germanium and arsenic are fourth-period elements in adjacent groups, and that the reduction of other Group V–B halides with zinc and hydrochloric acid has not been reported.

2. *Hydrolysis of tetrahydrides of the elements in group IV–B*

In contrast to the stability of methane to hydrolysis, silane reacts rapidly and quantitatively with water containing a trace of hydroxyl ion as catalyst. The reaction apparently proceeds by the co-ordination of hydroxyl ions to silicon, which has a maximum covalency of six, followed by the formation of molecular hydrogen from the protons of water and the hydrogen atoms at the negative end of the polar silicon–hydrogen bond. Methane, silane, germane, and stannane react very slowly, if at all, with pure water. Germane is unattacked by 33 per cent alkali, and stannane is undecomposed by 15 per cent caustic soda.[7] The inertness of methane is explained first by the unavailability of orbitals permitting the preliminary co-ordination of water, and second, by the lack of a tendency for the protons of water to unite with the slightly positive hydrogen atom bound to the more electronegative carbon atom. The stability of germane and stannane is not due to the impossibility of a pentacovalent or hexacovalent intermediate, but could be explained[3] if the germanium–hydrogen and tin–hydrogen bonds were either non-polar or were positive at the hydrogen end. Ignoring energy considerations for the moment, this explanation implies that the electronegativity values of germanium and tin are greater than that of silicon.

3. *Ammonolysis and hydrolysis of group IV–B halides*

Most carbon halides are not readily hydrolysed, but they form amines through an ammonium salt intermediate upon heating. In sharp contrast, silicon halides react rapidly and completely with water and with ammonia ultimately to form silica and silicon imide, respectively.[8] The hydrolysis of germanium halides is slow and readily reversible.[9,10,11] The reactivity of the germanium halides with ammonia is intermediate between that of the silicon and tin halides.[10,12] Organotin halides form addition compounds with ammonia instead of reacting at the tin–halogen bond,[13] but dimethyltin dichloride is 10·5 per cent hydrolysed in a 0·063 M aqueous solution

[6] R. WEST *J. Amer. chem. Soc.* **75**, 6080 (1953).
[7] H. J. EMELÉUS and J. S. ANDERSON *Modern Aspects of Inorganic Chemistry* Second Edition, p. 286. Van Nostrand, New York (1952).
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[10] C. A. KRAUS and L. S. FOSTER *J. Amer. chem. Soc.* **49**, 457 (1927).
[11] E. G. ROCHOW and A. L. ALLRED *J. Amer. chem. Soc.* **77**, 4489 (1955).
[12] C. A. KRAUS and E. A. FLOOD *J. Amer. chem. Soc.* **54**, 1635 (1932).
[13] C. A. KRAUS and W. N. GREER *J. Amer. chem. Soc.* **45**, 3078 (1923).

and is considerably dissociated into $(CH_3)_2Sn(H_2O)_n^{++}$ ions.[14] Lead tetrachloride hydrolyses and also forms some lead dichloride and chlorine.[15]

An investigation of dilute aqueous solutions of dimethylgermanium dichloride indicated that the equilibrium in the reaction

$$(CH_3)_2GeCl_2 + 2H_2O \rightleftharpoons (CH_3)_2Ge(OH)_2 + 2H^+ + 2Cl^-$$

is far to the right. The van't Hoff *i* factor is five, and the pH agrees well with that calculated from twice the molarity of dimethylgermanium dichloride.[11] On the other hand, the hydrolysis of dimethyltin dichloride according to the equations

$$(CH_3)_2SnCl_2 + nH_2O \rightleftharpoons (CH_3)_2Sn(H_2O)^{2+} + 2Cl^-$$

and

$$(CH_3)_2Sn(H_2O)^{2+} + H_2O \rightleftharpoons (CH_3)_2Sn(H_2O)_{n-1}OH^+ + H_3O^+$$

is not complete.[14] For a 0·0639 M solution, the van't Hoff *i* factor is 2·86, and the pH shows only about 10 per cent hydrolysis. The behaviour of $(CH_3)_2M(H_2O)_n^{2+}$ and $(CH_3)_2M(H_2O)_{n-1}(OH)^+$ is an indication that the electronegativities of germanium and tin are not equal as commonly accepted. The $>$GeOH group has a stronger tendency to release a proton than the $>$SnOH group, as is shown by the above pH measurements and by titrations of aqueous solutions of dimethylgermanium dichloride and of dimethyltin dichloride with solutions of sodium hydroxide.[11,14]

4. *Oxidation of the hydrides of the group IV–B elements*

Germane is more stable to oxidation than silane, but much less so than methane. Germane with excess oxygen in a closed system at 180°C is slowly oxidized,[16] while monosilane and the higher silanes react explosively in the air.

5. *Reaction of organolithium compounds with* $(C_6H_5)_3MH$

Triphenylmethane and triphenylgermane react differently from triphenylsilane and triphenylstannane with organolithium compounds. Triphenylmethane reacts according to the equation.[17]

$$(C_6H_5)_3CH + RLi \rightleftharpoons (C_6H_5)_3CLi + RH$$

Triarylsilanes react with organolithium compounds to form tetrasubstituted silanes and lithium hydride[18] regardless of the order of addition:

$$R_3SiH + R'Li \rightleftharpoons R_3SiR' + LiH$$

Analogously, the addition of a solution of phenyllithium to triphenylstannane yields tetraphenyltin and lithium hydride.[18] The main products obtained from the addition of a dilute ether solution of triphenylgermane to a solution of phenylithium are tetraphenylgermane and lithium hydride.[19] If the order of addition is reversed, the principal product is hexaphenyldigermane. The following sequence of reactions was

[14] E. G. ROCHOW and D. SEYFERTH *J. Amer. chem. Soc.* **75**, 2877 (1953).
[15] N. V. SIDGWICK *The Chemical Elements and Their Compounds I* p. 605. Clarendon Press, Oxford (1950).
[16] H. J. EMELÉUS and E. R. GARDNER *J. chem. Soc.* 1900 (1938).
[17] H. GILMAN and R. V. YOUNG *J. org. Chem.* **1**, 315 (1936).
[18] H. GILMAN and H. W. MELVIN, JR. *J. Amer. chem. Soc.* **71**, 4050 (1949).
[19] O. H. JOHNSON and D. M. HARRIS *J. Amer. chem. Soc.* **72**, 5566 (1950).

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suggested and later confirmed[20] for the formation of the hexaphenyldigermane:

$$(C_6H_5)_3GeH + C_6H_5Li \rightleftharpoons (C_6H_5)_3GeLi + C_6H_6$$

$$(C_6H_5)_3GeLi + (C_6H_5)_3GeH \rightleftharpoons (C_6H_5)_3GeGe(C_6H_5)_3 + LiH$$

This mechanism implies that the tertiary hydrogen in triphenylgermane, as in triphenylmethane, is more acidic than the corresponding hydrogen atoms in triphenylsilane and triphenylstannane. This order is consistent with the electronegativity of germanium being greater than that of silicon and tin. Triphenylplumbane is too unstable for a comparable investigation.[21]

6. *Variations in heat of formation of compounds of the group IV–B elements*

Table 1 indicates that the heats of formation, ΔH_f, of analogous compounds of the Group IV–B elements tend to alternate with the number of the period as shown by Fig. 1. This alternation is not predicted by considerations of PAULING's electronegativity scale and of ionic and convalent bond character. In general, the free energy of formation of gaseous compounds is the best thermodynamic quantity for measuring chemical affinity, but unfortunately, thermodynamic data are sparse. However, the energies of bonds in the halides and oxides of the Group IV–B elements are independent of the heats of atomization of these elements,[22] and hence, the ΔH_f^0 data are reasonably informative.

TABLE 1.—$\Delta H^0_{formation}$ IN kcal/mol[23]

	State	C	Si	Ge	Sn	Pb
MCl_4	l	− 33·3	− 153·0	− 130·0	− 130·3	− 78·85[24]
MCl_4	g	− 25·5	− 145·7	− 122	—	—
MBr_4	g	12	− 86·1[25]	− 68·7[23]	—	—
MBr_4	l	—	− 95·1	− 78·5[26]	− 94·1	—
MO_2	s	—	− 205·4	− 128·3	− 138·8	− 66·12
MO		− 26·42(g)	− 26·72(g)	− 22·8(g)	− 68·4(s)	− 52·4(s)
$M(CH_3)_4$	g	− 39·7[26]	− 69[27]	—	− 13·6[28]	3·2[28]
MO	ΔF^0:	− 32·81(g)	− 32·77(g)	− 28·2(g)	− 61·5(s)	− 45·3(s)

Summary of chemical observations. The general order of electronegativity indicated in these six examples seems to be carbon > germanium > silicon ≃ tin, instead of carbon > silicon > germanium = tin, as proposed by PAULING and generally accepted from early considerations of the periodic table.

It must be emphasized that electronegativity cannot be used exclusively to correlate and predict chemical behaviour. Within each series of analogous compounds discussed

[20] H. GILMAN and C. W. GEROW *J. Amer. chem. Soc.* **78**, 5435 (1956).
[21] H. GILMAN and J. C. BAILIE *J. Amer. chem. Soc.* **61**, 731 (1939).
[22] E. C. BAUGHAN *Quart. Rev.* **7**, 103 (1953).
[23] Unless indicated otherwise, these are from F. D. ROSSINI *et al. Selected Values of Chemical Thermodynamic Properties* (Circular 500 of the National Bureau of Standards), U.S. Government Printing Office, Washington, D.C. (1952).
[24] F. YA KULHA *J. Gen. Chem. U.S.S.R.* (English Translation) **24**, 1677 (1954).
[25] D. F. EVANS and R. E. RICHARDS *J. chem. Soc.* 1292 (1952).
[26] American Petroleum Institute Research Project 44, *Selected Values of Properties of Hydrocarbons* 3, National Bureau of Standards, U.S. Government Printing Office, Washington, D.C.
[27] S. TANNENBAUM *J. Amer. chem. Soc.* **76**, 1027 (1954).
[28] E. R. LIPPENCOTT and M. C. TOBIN *J. Amer. chem. Soc.* **75**, 4141 (1953).

in this section, there were also variations of many other properties, including bond length, state of matter, crystal structure, resonance stabilization, solubility, solvation, and steric hindrance. In reality, no series of elements forms a series of compounds in which only electronegativity varies. The change in free energy, ΔF, corresponding to a given reaction can then be considered to be determined by many factors. Furthermore, the reactions which are observed for chemical systems depend not only upon changes of free energy, but also on rates and mechanisms. A scale of electronegativity based on only chemical observations would be quite inaccurate, in view of the above

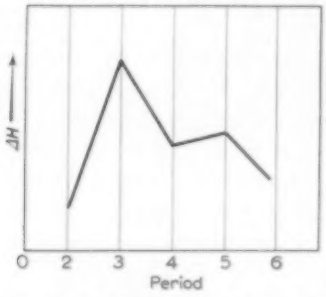


FIG. 1.—Variation of heat of formation with the period number of the group IV-B element.

complications. The remaining sections in this paper will describe the evaluation of electronegativity from certain physical measurements with the exclusion (as far as possible) of contributions from sources other than electronegativity.

NUCLEAR MAGNETIC RESONANCE

The frequency, ν, of electromagnetic radiation required for nuclear magnetic resonance (NMR) is given by $\nu = (\mu/Ih)H$, where μ/Ih has a characteristic value for each nuclear species and H is the strength of the magnetic field at the nucleus. The change in the resonance condition caused by the chemical environment of the nucleus is termed the "chemical shift". For most nuclei, the relation between the frequency of resonance and electronic parameters is very complex. However, the hydrogen resonance frequency depends to a large extent on the density of electrons close to the nucleus. Several observers[29,30,31,32,33] have reported the tendency of the chemical shift of hydrogen to reflect the electron-withdrawing ability of substituent atoms and groups.

We have discussed elsewhere the parameters which are responsible for chemical shift.[33] It was pointed out that the relative electronegativities of certain elements were linearly related to the chemical shifts in analogous compounds of the elements at infinite dilution in inert, magnetically isotropic solvents. In the series, XCH_3, the electron density around hydrogen and the chemical shift of hydrogen should increase with decreasing electronegativity of X. The chemical shifts of each of the methyl halides were determined at varying concentrations in carbon tetrachloride, and then

[29] H. S. GUTOWSKY and C. J. HOFFMAN *J. chem. Phys.* **19,** 1259 (1951).
[30] H. S. GUTOWSKY, D. W. MCCALL, B. R. MCGARVEY and L. H. MEYER *J. Amer. chem. Soc.* **74,** 4809 (1952).
[31] L. H. MEYER, A. SAIKA and H. S. GUTOWSKY *J. Amer. chem. Soc.* **75,** 4567 (1953).
[32] B. P. DAILEY and J. N. SHOOLERY *J. Amer. chem. Soc.* **77,** 3977 (1955).
[33] A. L. ALLRED, Thesis, Harvard University, 1956.

the chemical shift at infinite dilution was obtained by extrapolation. The linear variation of the extrapolated chemical shift values, ($CH_3 - H_2O$) in cycles, with electronegativity[34] is apparent in Fig. 2.

The successful correlation of the chemical shifts of the methyl halides prompted an investigation of the controversial electronegativities of the Group IV–B elements by NMR. In a series of compounds containing an M—C—H linkage (where M represents an element from Group IV–B), the density of electronic charge surrounding

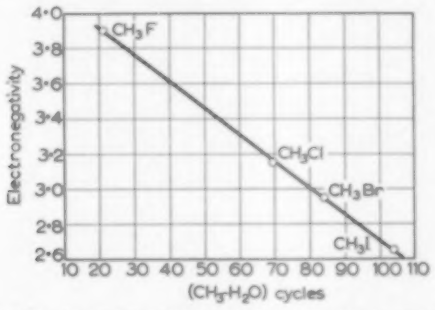
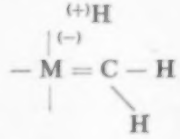


FIG. 2.—Chemical shifts of methyl halides at infinite dilution in carbon tetrachloride versus electronegativity of the halogens.

the proton increases as the electronegativity of M decreases, provided there are no major changes in hybridization as M is varied. The tetramethyl derivatives of the Group IV–B elements were selected for this investigation because there are supposedly uniform sp^3 hybrid bonds in these compounds. The contribution from hyperconjugation, involving the canonical form,



is assumed to be negligible. However, this assumption may not be necessary for the interpretation of the chemical shifts in this system, since the electron transfer in the canonical form involving hyperconjugation is toward the IV–B element and, therefore, augments the electronegativity of M in the M-carbon bond. In other words, if hyperconjugation is present, the electron-withdrawing ability of M in the π-bond as in the σ-bond decreases the electron density around the proton and thereby decreases the chemical shift. Furthermore, hyperconjugation, if present at all, would be expected to be approximately equally important in compounds of silicon, germanium, tin and lead, since all have similar *d* orbitals available.

EXPERIMENTAL

Tetramethylsilane, tetramethylgermane, and tetramethyltin were prepared from the corresponding chlorides and methylmagnesium bromide. Tetramethylmethane (99·81 per cent) was purchased from the Phillips Petroleum Company. Tetramethyllead was kindly supplied by the Ethyl Corporation, to whom we are grateful.

[34] M. L. HUGGINS *J. Amer. chem. Soc.* **75**, 4123 (1953).

The sample cells were prepared as follows: A glass capillary, 1·1–1·8 mm o.d., was filled with water which was the reference compound, sealed, and placed inside a 5 mm o.d. cylindrical Pyrex tube. The 5 mm tube was filled to a height of 4·5 to 5·0 cm with the sample and sealed.

The NMR spectra were obtained with a Varian Associates V-4300 B high resolution nuclear magnetic resonance spectrometer in conjunction with a 12 in. electromagnet system and an air turbine sample spinner. All of the spectra were

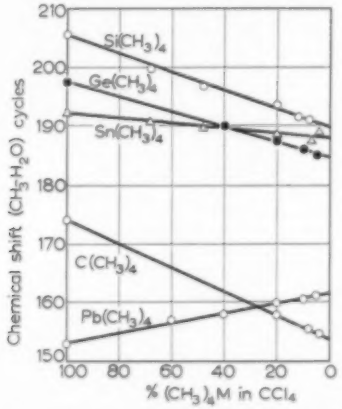


FIG. 3.—The hydrogen chemical shift of the tetramethyl group IV–B compounds as a function of their concentration in carbon tetrachloride.

obtained at room temperature and a frequency of 40 mc. For measuring the difference in cycles of the NMR signals from the sample and from the reference, the side-band technique of ARNOLD and PACKARD[35] was adopted. Chemical shifts are reported as the resonance frequency of the methyl group minus the resonance frequency of water ($CH_3 - H_2O$), and therefore, increasing positive values of chemical shifts correspond to increasing applied fields if the radiofrequency is constant. The accuracy of all measurements is estimated to be within $\pm 0{\cdot}7$ cycle.

The hydrogen NMR spectra of the tetramethyl Group IV–B compounds were observed in the pure liquid state and in solutions in carbon tetrachloride, and the results are presented in Fig. 3. The chemical shifts extrapolated to infinite dilution are 153·9 for tetramethylmethane, 189·8 for tetramethylsilane, 184·7 for tetramethylgermane, 188·0 for tetramethyltin, and 161·5 for tetramethyllead.

The chemical shifts exhibited by these compounds at infinite dilution in an inert, magnetically isotropic, solvent are considered to be a function only of the electron-withdrawing power of the Group IV–B elements.[33] Since the hybridization of bonding orbitals in halogen–carbon bonds differs from that in the IV–B element-carbon bonds, the electronegativities of the IV–B elements relative to the electronegativities of the halogens cannot be obtained by a direct comparison of the proton chemical shifts of the methyl IV–B compounds relative to the methyl halides. However, *relative* electronegativities within the IV–B Group were determined as follows: Carbon and silicon were assigned the electronegativity values, 2·60 and 1·90 respectively. These values were proposed by HUGGINS[34] and are comparable to

[35] J. T. ARNOLD and M. E. PACKARD *J. chem. Phys.* **19**, 1608 (1951).

PAULING's assignments of 2·5 to carbon and 1·8 to silicon. These relative values are predicted by practically all methods of measuring electronegativity, and also by chemical observations, provided in each case that the hybridization of orbitals is the same for carbon and silicon. The electronegativities of carbon and silicon were plotted in Fig. 4 as a function of the extrapolated proton chemical shifts of tetramethylmethane and tetramethylsilane; in so doing it was assumed that the chemical shift of the methyl derivatives is a linear function of electronegativity, as appears for

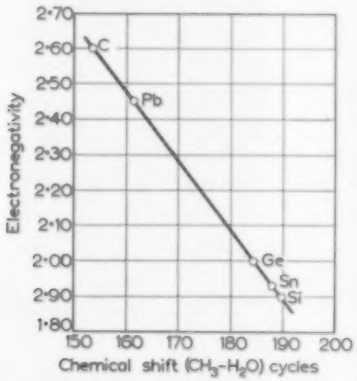


FIG. 4.—Chemical shift of $(CH_3)_4M$ at infinite dilution in carbon tetrachloride versus the electronegativity of M.

the halogens. The relative electronegativities of germanium, tin and lead were then determined by *interpolation*, using the corresponding chemical shifts of their tetramethyl derivatives in infinitely dilute solutions of carbon tetrachloride.

It should be pointed out that chemical shift may not be an exactly linear function of electronegativity in this case. However, it is obvious that the variation should be monotonic, and that a departure from linearity, if the variation is monotonic, would not change the order of electronegativities of the Group IV–B elements deduced by this method.

According to the above interpretation of the NMR data, the relative values of electronegativity of the IV–B elements in their tetramethyl compounds are 2·60 for carbon, 1·90 for silicon, 2·00 for germanium, 1·93 for tin, and 2·45 for lead. These values are not predicted by general interpretations of Mendeléeff's periodic table and differ considerably from PAULING's values,[2] 2·5 for carbon, 1·8 for silicon, 1·7 for germanium, and 1·7 for tin. However, the order of electronegativities found by NMR is consistent with the chemical observations discussed in the previous section.

NUCLEAR QUADRUPOLE RESONANCE

A nucleus with spin number greater than half will possess an electric quadrupole moment, Q. The property, Q, is considered to measure the departure of the nuclear charge from spherical symmetry. If $Q \neq 0$, the charge is symmetrical about the axis of spin, but either flattened ($Q < 0$) or elongated ($Q > 0$). An electric quadrupole moment will not interact with a uniform electric field, but in a static electric field gradient, an interaction occurs giving rise to different energy levels of the nucleus.

The energy of the nucleus in the latter case depends upon the orientation of the nucleus with respect to the electric field. Transition between the possible orientations of a nucleus ($Q \neq 0$) in an inhomogeneous electric field can be induced by an oscillating magnetic field of suitable radiofrequency. This reorientation phenomenon is termed "nuclear quadrupole resonance." By measuring the radiofrequency and Q, one can determine q, the inhomogeneity of the electric field at the nucleus due to the electrons and other nuclei in the molecule. For some molecules eQq, the nuclear quadrupole coupling constant, can be obtained from the hyperfine structure of microwave spectra.

Information about the electron distribution of molecules should be obtainable from q. The electric field at the nucleus is the sum of contributions from all other nuclei and electrons. However, the asymmetry of the electric field at the nucleus is caused largely by unfilled p orpitals.[36,37] Since q is proportional to $1/r^3$ for a charge at a distance r from a nucleus,[36] penetrating electrons make the major contribution to eQq. Calculations show that for chlorine the contribution of an electric charge 1 Å from the nucleus is 0·5 per cent of that from a p electron.[37] Filled shells and s electrons do not produce an asymmetric electric field at the nucleus due to spherical symmetry.[36] The contribution of d electrons is difficult to evaluate,[38] but probably is small due to non-penetration. The effect of neighboring atoms is relatively small, and for similar compounds having the same crystal structure it may be assumed to be constant.[38]

For the halogens, eQq is zero for the halide ions (which have closed shells), large for the isolated atoms (which have vacant p-orbitals), and intermediate in compounds in which the halogen is covalently bonded to a more electropositive element. TOWNS and DAILEY[36] pointed out that increasing s character by hybridization decreases eQq due to increasing spherical symmetry. Also, double bond formation involving donation of an unshared p pair of the halogen lowers the eQq value. To date, the above effects on eQq have not been conclusively disentangled. However, considerable electric quadrupole coupling data on halogen compounds have accumulated, and attempts have been made to obtain a correlation with the electronegativities of bonded atoms.

MAYS and DAILEY[39] obtained eQq for chlorine and bromine in MH_3X (M = C or Si, and X = Cl or Br) from microwave data and interpreted their data in terms of "unbalanced" p electrons according to the approach of TOWNS and DAILEY.[36] The value of eQq for one unbalanced electron was taken from atomic beam measurements and for no unbalanced electrons, as in halide ions, was assumed to be zero. The eQq values for pure single and double bonds were calculated, the percentage of s characters assigned, and then the percentages of double bond, single covalent bond, and ionic bond characters were estimated.

LIVINGSTON[40] plotted the eQq values of forty-one chlorine-containing compounds as a function of the electronegativity difference between chlorine and the bonded atom and observed a general decrease of eQq with electronegativity difference, or increasing ionic character.

[36] C. H. TOWNS and B. P. DAILEY *J. chem. Phys.* **17,** 782 (1949).
[37] C. H. TOWNS and B. P. DAILEY *J. chem. Phys.* **20,** 35 (1952).
[38] B. P. DAILEY *Disc. Faraday Soc.* **19,** 255 (1955).
[39] J. M. MAYS and B. P. DAILEY *J. chem. Phys.* **20,** 1695 (1952).
[40] R. LIVINGSTON *J. phys. Chem.* **57,** 496 (1953).

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SCHAWLOW[41] assumed that if a halogen bond could be represented as some mixture of pure ionic and pure covalent structures, the percentage of covalent bond character, f, would be equal to $100(\nu/\nu_0)$, where ν is the observed nuclear quadrupole resonance frequency and ν_0 was determined by atomic beam measurements and is approximately equal to the frequency of pure quadrupole resonance in the halogen molecule. For the *p*-dihalobenzenes, f was found to increase with decreasing electronegativity difference, $(\chi_x - \chi_c)$ (PAULING's values[1]), in the carbon–halogen bond. However, when the Group IV–B element was varied, f did not increase monotonically with decreasing $(\chi_x - \chi_m)$. SCHAWLOW did not consider the low value of f for the silicon halides to be due to greater ionic character of the silicon–halogen bond, which would imply that the electronegativities of germanium and tin are greater than that of silicon. Instead, he attributed the low values to more complicated structures and used older methods[36,39] to calculate bond character from eQq. The calculations gave the surprisingly high values of 45 ± 12 and 60 ± 15 per cent double-bond character in silicon tetrachloride and silicon tetrabromide, respectively.

GORDY[42,43] proposed that for MX_n, eQq of X, a halogen, is related to the electronegativity difference, $(\chi_x - \chi_m)$, by the relation

$$U_p = \frac{eQq \text{ mol}}{2eQq \text{ atom}} = a + b(\chi_x - \chi_m)$$

where U_p is the number of "unbalanced" p electrons and eQq is determined for the halogen by atomic beam methods. This relation was followed, with some scattering of points. The deviation of silicon halides (or germanium and tin halides) was taken as evidence of silicon double bonds.

More recently, GORDY[44] made another attempt to evaluate bond character in the Group IV–B halides from eQq values. Some objections[38,45,46,47] have been made to his assumptions. He found that the net effect of the ionic and double-bond contributions was a fraction of a positive charge, c, on the Group IV–B element. The relation between electronegativity and effective nuclear charge, which was also proposed by GORDY[48] and which is discussed in the section on electronegativity and electrostatics, was modified to $\chi = 0{\cdot}31(n + 1 + c/r + 0{\cdot}50)$, where n is the number of electrons in the valence shell and r is the covalent radius. The "effective" electronegativities of the Group IV–B elements were calculated by GORDY and are reproduced in Table 2. An alternation in electronegativity is observed from carbon to tin.

TABLE 2.—"EFFECTIVE" ELECTRONEGATIVITY OF M^{IV}

CCl_4	2·58	$SiCl_4$	2·04	$GeCl_4$	2·08	$SnCl_4$	1·97
CBr_4	2·55	$SiBr_4$	1·98	$GeBr_4$	2·03	$SnBr_4$	1·91
CI_4	2·50	SiI_4	1·96	GeI_4	2·00	SnI_4	1·87

[41] A. L. SCHAWLOW *J. chem. Phys.* **22**, 1211 (1954).
[42] W. GORDY *J. chem. Phys.* **19**, 792 (1951).
[43] HUGH ROBINSON, H. C. DEHMELT, and W. GORDY *J. chem. Phys.* **22**, 511 (1954).
[44] W. GORDY *Disc. Faraday Soc.* **19**, 14 (1955).
[45] B. P. DAILEY and C. H. TOWNS *Disc. Faraday Soc.* **19**, 274 (1955).
[46] B. P. DAILEY and C. H. TOWNS *Disc. Faraday Soc.* **19**, 278 (1955).
[47] B. P. DAILEY and C. H. TOWNS *Disc. Faraday Soc.* **19**, 279 (1955).
[48] W. GORDY *Phys. Rev.* **69**, 604 (1946).

The above investigations indicated that for a series of compounds containing an M–X linkage, in general, as the electronegativity of X decreases, the bond becomes more ionic, and the value of eQq decreases from that of a halogen atom to zero for a halide ion. The variation is approximately linear for electronegativity differences between 0 and 1·8.[44]

The electric quadrupole coupling constants of the halogens in the five series, MCl_4, MH_3Cl, MBr_4, MH_3Br, and MI_4, are plotted as a function of electronegativity difference in Fig. 5–9. Also in each figure, the quadrupole coupling constant of the corresponding halogen molecule is plotted. For the halogen molecules, the eqQ values were obtained from atomic beam measurements[49] and the electronegativity differences are of course zero. The eqQ values, recorded in Table 3, were obtained

TABLE 3

	eqQ (Mc/sec)	Reference		eqQ (Mc/sec)	Reference
CCl_4^{35}	81·85	41	CBr_4^{79}	536·0	42
$SiCl_4$	40·97	41	$SiBr_4$	295·1	42
$GeCl_4$	51·32	41	$GeBr_4$	351·5	42
$SnCl_4$	48·20	41	$SnBr_4$	329·0	42
CH_3Cl	75·13	50	CI_4^{127}	2130·33	44
SiH_3Cl	40·0	40	SiI_4	1329·055	44
GeH_3Cl	46	40	GeI_4	1492·458	44
			SnI_4	1389·307	44
CH_3Br^{79}	577·0	50	Cl_2^{35}	109·746	42
SiH_3Br	336	51	Br_2^{79}	768·8[a]	42
GeH_3Br	380	40	I^{127}	2292·430	42

[a] eqQ in reference 41 is 384·4 Mc/s and is, we believe, one-half of the correct value. However, we have been unable to find the stated value of eQq for Br_2 elsewhere in the literature.

from microwave spectra for MH_3Cl and MH_3Br and from pure quadrupole spectra of solids for MCl_4, MBr_4, and MI_4. The spectra of each MX_4 series, with the exception of methyl iodide, contained more than one line and were identical, indicating isomorphous crystals and a constant contribution to eqQ by solid state interactions. The eqQ value corresponding to the average frequency was chosen. As shown by Fig. 6, 8, and 9, the eqQ values of the halogen molecules do not follow exactly the trends established by the MX_4 compounds, probably due to solid state interactions in the latter case. The electronegativity values employed in Fig. 5–9 are: chlorine 3·15, bromine 2·95, iodine 2·65, carbon 2·60, silicon 1·90, germanium 2·00, and tin 1·93, and were the ones that were either assigned or determined in the course of NMR experiments. The best straight line was constructed for the co-ordinates determined by these values of eqQ and *relative* electronegativity.

The approximately linear relations shown by Fig. 5–9 between the quadrupole coupling constant and electronegativity difference may be attributed either to the electronegativity order carbon > germanium > tin > silicon, or to a different electronegativity order (say of PAULING, carbon > silicon > germanium = tin) and

[49] W. GORDY, J. W. SIMMONS and A. G. SMITH *Phys. Rev.* **74**, 243 (1948).
[50] A. H. SHARBAUGH, J. K. BRAGG, T. C. MADISON and R. L. THOMAS *Phys. Rev.* **76**, 1419 (1949).

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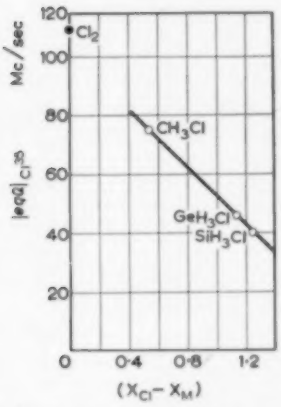

FIG. 5.—Quadrupole coupling constants of chlorine in MH_3Cl versus the difference of the electronegativities of chlorine and M.

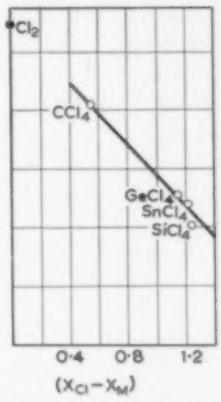

FIG. 6.—Quadrupole coupling constants of chlorine in MCl_4 versus the difference of the electronegativities of chlorine and M.

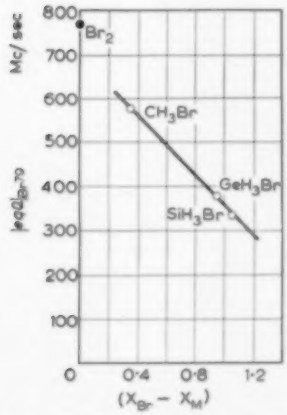

FIG. 7.—Quadrupole coupling constants of bromine in MH_3Br versus the differences of the electronegativities of bromine and M.

FIG. 8.—Quadrupole coupling constants of bromine in MBr_4 versus the difference of the electronegativities of bromine and M.

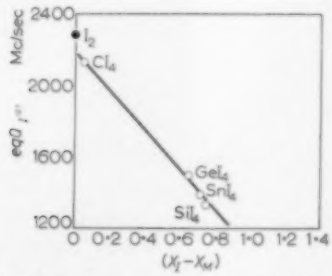

FIG. 9.—Quadrupole coupling constants of iodine in MI_4 versus the difference of the electronegativities of iodine and M.

different relative contributions of *s*-hybridization and double bonding for silicon and for germanium and tin. The first possibility is highly probable since the electronegativity order, carbon > germanium > tin > silicon, is found by nuclear magnetic resonance measurements of inductive effects in the compounds $M(CH_3)_4$ in which the extent of *s*-hybridization is constant and there is no multiple bonding to M, with the possible exception of a small contribution due to hyperconjugation.

From the investigations of nuclei in molecules by nuclear magnetic resonance spectroscopy and nuclear quadrupole spectroscopy, it is concluded that the order of electronegativities of the Group IV–B elements in identical valence states is carbon > germanium > tin > silicon.

ELECTRONEGATIVITY FROM THERMOCHEMICAL DATA

PAULING[1] found empirically that the energy of the bond A—B is generally greater than, or equal to, the average of the bond energies of A—A and B—B. The difference, Δ, between the actual bond energy of A—B and the average energy, termed "normal covalent energy" of the corresponding homatomic bonds was designated as the "additional ionic resonance energy" and expressed

$$\Delta = D(A—B) - \tfrac{1}{2}[D(A—A) + D(B—B)] \quad (1)$$

PAULING pointed out that Δ increases as atoms A and B become more unlike with respect to electronegativity, and related the square root of Δ to electronegativities by

$$(\chi_A - \chi_B) = 0{\cdot}208\sqrt{\Delta} \quad (2)$$

The elements were assigned electronegativity values such that their differences were approximately equal to the square roots of the Δ values in electron volts. Since the values of many homatomic bond energies and heats of formation of gaseous compounds are unknown, Δ cannot be obtained for most bonds by using equation (1). PAULING proposed that for the compounds MX_n

$$\Delta = \frac{Q_{\text{formation}}}{n} \quad (3)$$

Equation (3) involves the approximation that the contributions by van der WAALS interaction and other factors to the heats of formation of the reacting elements and the product are equal.

Since the original electronegativity scale was established by PAULING, more accurate and additional thermochemical data have accumulated and recalculations have been made by HUGGINS[34] and by H. O. PRITCHARD and H. A. SKINNER.[2] Another evaluation appears desirable since part of HUGGINS' data should be revised and since PRITCHARD and SKINNER did not assign electronegativity values from their thermal data.

Data and calculations

In this investigation, thermal data were taken from *Selected Values of Chemical Thermodynamical Properties*[22] with the following exceptions, which are taken from the indicated references (standard values in kcal/mol and at 298°K unless stated

[51] L. BREWER and R. F. PORTER *J. chem. Phys.* **21**, 2012 (1953).

otherwise): $\Delta H_{\text{sub Si}} = 89{\cdot}9$[22] $\Delta H_{\text{sub Ge}} = 89{\cdot}2$;[22] $\Delta H_{\text{sub grey Sn}} = 70{\cdot}0$[51] $\Delta H_{\text{sub CF}_4}$ estimated to be 2 from $\Delta H_{\text{fus}}^{89{\cdot}47} = 0{\cdot}167$ and $\Delta H_{\text{vap}}^{145{\cdot}14} = 3{\cdot}01$; $\Delta H_{\text{fus CCl}_4}^{298}$ assumed equal to $\Delta H_{\text{fus}}^{250{\cdot}3}$; $\Delta H_{\text{formation C(CH}_3)_4}^{298} = -39{\cdot}67$;[26] $\Delta H_{\text{sub SiF}_4}$ estimated to be 6 from $\Delta H_{\text{sub}}^{177{\cdot}7} = 6{\cdot}15$; $\Delta H_{\text{fus SiCl}_4}^{298}$ estimated to be 1·8 from $\Delta H_{\text{fus}}^{205} = 1{\cdot}84$; $\Delta H_{\text{fus SiBr}_4}$ estimated to be 2 from an average of $\Delta H_{\text{fus of CBr}_4 \text{ and SnBr}_4}$; $\Delta H_{\text{form SiBr}_4\text{(gas)}} = -100{\cdot}7$;[25] $\Delta H_{\text{form SiI}_4\text{(gas)}} = -47{\cdot}7$;[25] $\Delta H_{\text{fus Si(CH}_3)_4\text{(gas)}} = -6{\cdot}9$;[27] $\Delta H_{\text{vap SiCl}_4}^{298}$ assumed equal to $\Delta H_{\text{vap}}^{356{\cdot}3}$; $\Delta H_{\text{fus GeCl}_4}$ estimated to be 2 from an average of $\Delta H_{\text{fus SiCl}_4}$ and $\Delta H_{\text{fus SnCl}_4}$; $\Delta H_{\text{form GeBr}_4\text{(gas)}} = -83{\cdot}3$;[25] $\Delta H_{\text{form GeBr}_4\text{(liq)}} = -78{\cdot}5$;[25] $\Delta H_{\text{fus GeBr}_4}$ estimated to be 3 from an average of $\Delta H_{\text{fus SiBr}_4}$ and $\Delta H_{\text{fus SnBr}_4}$; $\Delta H_{\text{form GeI}_4\text{(gas)}} = -42{\cdot}0$;[25] $\Delta H_{\text{form GeI}_4\text{(solid)}} = -30{\cdot}5$;[25] $\Delta H_{\text{vap SnCl}_4}^{298}$ assumed equal to $\Delta H_{\text{vap}}^{389}$; $\Delta H_{\text{fus SnCl}_4}^{298}$ assumed equal to $\Delta H_{\text{fus}}^{239{\cdot}9}$; $\Delta H_{\text{sub SnBr}_4}$ estimated to be 13 from $\Delta H_{\text{fus}}^{303} = 3$ and $\Delta H_{\text{vap}}^{478} = 10$; $\Delta H_{\text{form Sn(CH}_3)_4} = -13{\cdot}6$;[28] $\Delta H_{\text{form Pb(CH}_3)_4} = 3{\cdot}6$;[28] $\Delta H_{\text{form PbCl}_4} = -78{\cdot}85$;[24] and $\Delta H_{\text{fus PbCl}_4}$ assumed equal to $\Delta H_{\text{fus SnCl}_4}$ The energy of each homatomic bond of the Group IV–B elements was assumed to be one-half of the heat of atomization of the element from a tetrahedral lattice. HUGGINS' electronegativity values[31] of 2·20, 3·90, 3·15, 2·95, and 2·65 were assumed for hydrogen, fluorine, chlorine, bromine, and iodine, respectively. These relative values are obtained by most methods of measuring electronegativity and are widely accepted.

TABLE 4

Molecule	χ_M(A—B)	$\chi_M(Q_r/n)$	Molecule	χ_M(A—B)	$\chi_M(Q_r/n)$
CH_4	2·65	—	$SnCl_4$	2·00	1·93
CF_4	2·57	2·57	$SnBr_4$	1·92	1·92
CCl_4	2·59	2·54	$SnCl_2$	—	1·80
			$SnBr_2$	—	1·77
SiH_4	77·8	1·80	SnI_2	—	1·78
SiF_4	133·3	1·95			
$SiCl_4$	87·9	1·89	PbF_4	—	2·35
$SiBr_4$	70·7	1·91	$PbCl_4$	—	2·21
SiI_4	52·5	1·92	PbF_2	—	2·11
			$PbCl_2$	—	1·79
$GeCl_4$	2·00	1·95	$PbBr_2$	—	1·75
$GeBr_4$	2·00	2·01	PbI_2	—	1·70
GeI_4	1·98	2·08			

Calculations were restricted to molecules having all bonds identical, with the exception of 2,2-dimethylpropane, to avoid questionable assumptions about the relative contributions of different bonds to the heat of formation. The energy of a given bond may be different in different molecules. Assuming that D(C—H) = 99·5 kcal/mol as in methane, calculations of the M—C bond energies in $M(CH_3)_4$ showed that (a) D(C—C) is approximately the same as that calculated from ΔH^0 sub. of diamond (also calculated in reference (2)) (b) D(Si—C) leads to an abnormally high electronegativity for silicon (also calculated in reference (2)) and (c) D(Sn—C) and D(Pb—C) are negative.

Electronegativity values for the Group IV–B elements were calculated by the application of equations (1) and (2), and the results are presented in the columns

headed χ_M(A—B) in Table 4. Also, equations (1) and (3) were employed and the resulting electronegativity values are given in the column headed $\chi_M(Q_f/n)$ in Table 4. The average values for the Group IV–B elements from PAULING,[2] $\chi_{p'}$, from HUGGINS,[34] χ_H, and from the thermochemical calculations of this research, χ_M(A—B) and $\bar{\chi}_M(Q_f/n)$ are compiled in Table 5.

The value, $\Delta H^0_{\text{sublimation}} = 100$ kcal/at. wt. for silicon, was somewhat arbitrarily selected in reference[34] instead of the National Bureau of Standards value, $\Delta H^0_{\text{sublimation}} = 88{\cdot}0$ kcal/at. wt., so that the non-polar bond energy (and hence electronegativity) of silicon "would not be out of line with the other elements" of Group IV–B. This decision, based on the view that homatomic bond energies and electronegativities of the Group IV–B elements remain constant or decrease with increasing atomic number, obscured the order of electronegativity that was found in this investigation.

TABLE 5

	χ_P	χ_H	χ_M(A—B)	$\bar{\chi}_M(Q_f/n)$	
				M^{II}	M^{IV}
C	2·5	2·60	2·60	—	2·56
Si	1·8	1·90	1·89	—	1·93
Ge	1·7	1·90	1·99	—	2·01
Sn	1·7	1·90	1·96	1·78	1·93
Pb	—	—	—	1·84	2·23

In view of the approximations involved, the agreement in Tables 4 and 5 is excellent. An alternation in electronegativity going down the Table is observed in both sets of thermochemical calculations in this research. Also, the electronegativity is shown to increase with increasing valency. The high electronegativity for lead is surprising but is supported by nuclear magnetic resonance measurements.

ELECTRONEGATIVITY FROM ELECTROSTATICS

GORDY[48] proposed that electronegativity be defined "for a neutral atom in a stable molecule as the potential at a distance r (covalent radius) from the nucleus which is caused by the nuclear charge which is effective at that distance." The equation

$$\chi = 0{\cdot}31\frac{(n+1)}{r} + 0{\cdot}50$$

in which n is the number of valence electrons was used to calculate the electronegativities of fifty-two elements. In the derivation of this equation, it was assumed that electrons in closed shells exert full screening power on each other and that the screening constant of one valence electron for another is 0·5. Constants were selected to make the electrostatic potential scale coincide with PAULING's thermochemical scale. GORDY's electronegativity values for the Group IV–B elements, carbon 2·52, silicon 1·82, germanium 1·77, and tin 1·61, indicate a monotonic decrease of electronegativity with increasing period number.

PRITCHARD and SKINNER[2] employed SLATER's rules[52] to estimate the effective nuclear charge, Z_{eff}, and then used the relation (from GORDY),

$$\chi = a + b\frac{(Z_{eff})}{r}$$

to calculate electronegativities. However, it was necessary to fit different values for a and b for each row of the Periodic Table. PRITCHARD and SKINNER obtained the electronegativity values 2·51 for carbon, 1·84 for silicon, 1·87 for germanium, and 1·74 for tin.

Elsewhere[53] we have proposed a scale of electronegativity based on the calculated force of attraction between the nucleus and an electron from a bonded atom. The electronegativity values for forty-four elements were calculated using the equation,

$$\chi = 0{\cdot}359\frac{(Z_{eff})}{r^2} + 0{\cdot}744$$

in which Z_{eff} is determined by SLATER's rules, and n is the covalent radius. The electronegativity values, 2·50 for carbon, 1·74 for silicon, 2·02 for germanium, and 1·72 for tin from this relation are consistent with the NMR and most recent thermochemical values and with most chemical observations. For a discussion of the electrostatic force scale of electronegativity, see reference (53).

WORK FUNCTIONS

GORDY[54] discovered a correlation between the extent to which a metallic element in a compound attracts electrons and the energy required to release an electron from the pure metal by photoelectric or thermionic emission. A plot of work function (ϕ) in electron volts versus electronegativity indicated the relation

$$\chi = 0{\cdot}44\phi - 0{\cdot}15$$

The electronegativities of Group IV–B elements in the pure state were calculated using this relation and are given in Table 6.

TABLE 6

	Si	Ge	Sn (grey)	Sn (white)	Pb
Work function,[55] eV	4·1	4·56	4·38	4·51	4·02
Electronegativity	1·65	1·86	1·78	1·81	1·62

These work functions are mean values from many measurements by thermionic, photoelectric, threshold, and contact potential methods. The influence of impurities, temperature, allotropy, and anisotropy complicate the accurate determination of work functions. Diamond, the form of carbon comparable with that of silicon, germanium, and grey tin is a non-conductor and hence cannot be examined by any

[52] J. C. SLATER *Phys. Rev.* **36,** 57 (1930).
[53] A. L. ALLRED and E. G. ROCHOW *J. inorg. nucl. Chem.* **5,** 264 (1958).
[54] W. GORDY and W. J. O. THOMAS *J. chem. Phys.* **24,** 439 (1956).
[55] H. B. MICHAELSON *J. appl. Phys.* **21,** 536 (1950).

of the methods for measuring work functions listed above. The work function of grey tin (diamond lattice) is 0·12 eV greater than that of white tin (ditetragonal-bipyramidal lattice), and thus reflects the influence of crystal structure on the work function.

Despite the inapplicability of this method to carbon, it is useful for comparing the electronegativities of the remaining Group IV–B elements. Once again germanium is observed to be more electronegative than silicon, and tin is found to be intermediate between germanium and silicon. The low value for lead in comparison to the other elements might be attributable to its crystal structure (f.c.c.), which is very different from the diamond lattice encountered in the other elements of Group IV–B.

OTHER METHODS FOR EVALUATING ELECTRONEGATIVITY

In this research, an effort has been made to determine the electronegativity values of the elements in Group IV–B by the most precise methods available. A few previously proposed methods, of varying validity, for the correlation of electronegativity with certain physical properties have not been applied but will be discussed briefly in this section.

Dipole moments. MALONE[56] proposed that the dipole moment of a bond is proportional to the difference of the electronegativities of the bonded atoms. This method appears to be accurate for most diatomic molecules but fails in many other cases. The dipole moment of a bond is not usually a measure only of the ionic character, or the difference of electronegativities, since, as discussed by COULSON,[57] (a) hybrid bonding orbitals do not possess central symmetry and therefore, produce atomic dipoles, and (b) lone-pair electrons contribute to the total dipole moment.

Bond stretching force constants. WALSH[58] suggested that the electronegativity of an atom or Group A can be quantitatively defined as the stretching force constant of the bond between A and hydrogen. The stretching force constants of bonds between hydrogen and silicon, germanium and tin are not known to the degree of precision that would permit an estimation of the electronegativities of these elements of Group IV–B by WALSH's method.

GORDY[59] proposed the empirical relation

$$k = aN\left(\frac{\chi_A\chi_B}{d^2}\right)^{0.75} + b$$

where χ_A and χ_B are the electronegativities of atoms A and B in the bond A—B, k is the stretching force constant of the bond, N is the bond order, d is the bond length, and a and b are constants. Using this relation, GORDY calculated the electronegativity values 2·55 for carbon, 1·8 for silicon, 1·7 for germanium, 1·7 for tin, and 1·5 for lead.

"*Stability ratio*". SANDERSON[4,5,60] proposed that the electronegativity of an atom may be represented by its "stability ratio". The "stability ratio" was defined as "the ratio of the electron density (ED) of an atom or ion to the electron density $(ED)_i$ of an isoelectronic inert atom, real or hypothetical, and determined by interpolation between real values." SANDERSON determined the "average electron density" of an

[56] J. G. MALONE *J. chem. Phys.* **1**, 197 (1933).
[57] C. A. COULSON *Proc. roy. Soc.* A **207**, 63 (1951).
[58] A. D. WALSH *Proc. roy. Soc.* A **207**, 13 (1951).
[59] W. GORDY *J. chem. Phys.* **14**, 305 (1946).
[60] R. T. SANDERSON *J. chem. Educ.* **31**, 2 (1954).

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atom by dividing the atomic number by the volume which he calculated from the covalent radius. The term, "isoelectronic inert atom" refers to a non-existent "inert gas", which is isoelectronic with the atom of interest. The "covalent radii" of the isoelectronic inert atoms were determined by interpolation between "the covalent radii" of the real inert gases. Of course, inert gases do not form covalent bonds, and SANDERSON further assumed that for the inert gases, "the covalent radii" could be equated to the van der Waals radii in crystals.

The stability ratio combines a number of different physical measurements in order to arrive at an estimate of how tightly electrons are held in atoms. It is not based on a single theoretical approach, and it requires a number of controversial assumptions for its evaluation. However, stability ratios explain a large number of chemical observations[3] which appeared to be anomalous from considerations of previously established electronegativity scales. More particularly, the values of the stability ratios indicate that there is an alternation of electronegativity with increasing period number in Groups III–B to VI–B. Within each group, the electronegativity of the element in the fourth period exceeds that of the element in the third period, and the electronegativity of the element in the sixth period exceeds that of the element in the fifth period. PRITCHARD and SKINNER[2] have argued that the alternation of stability ratios is attributable to the alternation of the calculated electron densities of the inert gases. They also questioned the use of "collison radii" in the calculation of the electron densities of the inert gases, and pointed out that if more recent "radii" are used, the alternation practically disappears. SANDERSON's method gives the electronegativity values 2·47 for carbon, 1·74 for silicon, 2·31 for germanium, 2·02 for tin, and 2·37 for lead.

Ionization potentials and electron affinities. MULLIKEN[61,62] proposed that the "absolute" electronegativity of an atom is equal to the average of its ionization potential, I_A, and electron affinity, E_A. The values for I_A and E_A are not usually the physically observable quantities, but are calculated from the appropriate valence states. This method has been applied for the calculation of the electronegativities of thirty-two elements,[2] including carbon and silicon, but unfortunately, sufficient data for the extension of this method for germanium, tin, and lead do not appear to be available.

SUMMARY

The electronegativity values derived from this research, together with practically all of those reported in the scientific literature for the elements of Group IV–B, are compiled in Table 7. For methods which were applied to more than one series of compounds, the average value is given. In the light of the concept of orbital electronegativity, efforts have been made throughout this research to compare the electronegativities of the Group IV–B elements in analogous compounds in which the hybridization of bonding orbitals remains approximately constant. For methods based on properties which are insensitive to orbital characteristics, the invariant values are given.

A comparison can now be made of the electronegativity values determined for the elements of Group IV–B from the diverse physical properties: chemical shifts of nuclear magnetic resonance, nuclear quadrupole coupling constants, bond energies,

[61] R. S. MULLIKEN *J. chem. Phys.* **2**, 782 (1934).
[62] R. S. MULLIKEN *J. chem. Phys.* **46**, 497 (1949).

electrostatic potentials, electrostatic forces, and work functions. The qualitative and quantitative agreement of the scales from these methods is close as shown by Table 7, and lends confidence to the concept of electronegativity. From an examination of the scales which are based on the chemical shifts of nuclear magnetic resonance, nuclear quadrupole coupling constants, and bond energies (and which reflect the electronegativities of elements in analogous compounds), the general order of decreasing electronegativity is carbon > lead > germanium > tin > silicon. This order is consistent with the chemical observations listed earlier. From a consideration of the methods and values listed in Table 7, it is suggested that the "best" electronegativity values for the Group IV–B elements in sp^3 valence states are equal to those obtained from measurements of chemical shifts, and are 2·60 for carbon, 1·90 for silicon, 2·00 for germanium, 1·93 for tin, and 2·45 for lead.

TABLE 7.—SUMMARY OF THE ELECTRONEGATIVITY VALUES OF THE ELEMENTS OF GROUP IV–B

	C	Si	Ge	Sn	Pb
NMR (and NQR)	2·60	1·90	2·00	1·93	2·45
NQR (GORDY[44])	2·54	1·99	2·03	1·92	
Thermal data					
$\bar{\chi}$(A—B)	2·60	1·89	1·99	1·96	
$\bar{\chi}(Q_r/n)$	2·65	1·93	2·01	1·93	2·28
PAULING[1]	2·5	1·8	1·7	1·7	
HUGGINS[34]	2·60	1·90	1·90	1·90	
Electrostatics					
Zeff/r,2	2·50	1·74	2·02	1·72	
Zeff/r (GORDY[44])	2·52	1·82	1·77	1·61	
Zeff/r (PRITCHARD and S.[2])	2·51	1·84	1·87	1·73	
Work function		1·65	1·86	1·80	1·62
Force constant GORDY[59]	2·55	1·8	1·7	1·7	1·5
Stability ratio (SANDERSON[51])	2·47	1·74	2·31	2·03	2·37

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THE DIAMAGNETISM OF IRON DODECACARBONYL

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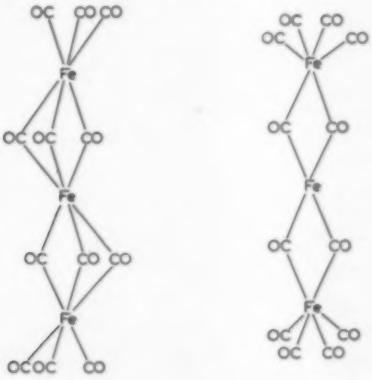
Abstract—In contrast to previous discussion of the structure of iron dodecacarbonyl, it is shown by means of molecular-orbital theory that the structure analogous to that of iron enneacarbonyl is diamagnetic and hence in accord with observation.

IN a preliminary communication[1] of X-ray examination of the above compound MILLS has suggested that two structures, I and II, are indicated; in particular, interest has been revived in structure I which is geometrically analogous to that of iron enneacarbonyl. Moreover, a further spectral investigation[2] gives support to a structure containing six bridge carbonyl groups rather than four.



I II

Although this structure (I) had been rejected previously by SHELINE,[3] the main reason being its apparent incompatibility with the observed diamagnetism of the dodecacarbonyl, it seems worthy of further consideration. In fact, it is the purpose of this note to show that molecular-orbital theory indicates a diamagnetic ground state for such a structure. Following the treatment of iron enneacarbonyl by DUNITZ and ORGEL,[4] we assume a local symmetry C_{3v} about the iron atom. After σ-bonding, three orbitals remain on each iron atom with symmetry $A_1 + E$ in the above point group, the A_1 being of a $d\sigma$ and the E of a mixed $d\pi/d\delta$* form with respect to the molecular axis. Consider now the complete molecule; after σ-bonding there are available three identical $A_1(d\sigma)$ orbitals (one per iron atom) and, similarly, three identical

* The author would like to thank the referee for pointing out the mixed nature of the E orbitals.

(1) O. S. MILLS *Chem. & Ind.* Rev.) (3, 73 (1957).
(2) F. A. COTTON and G. WILKINSON *J. Amer. chem. Soc.* 79, 752 (1957).
(3) R. K. SHELINE *Ibid.* 73, 1615 (1951).
(4) J. D. DUNITZ and L. E. ORGEL *J. chem. Soc.* 2594 (1953).

$E(d\pi/d\sigma)$ orbitals, and it is the interaction of these which will determine the magnetic properties of iron dodecacarbonyl. Now it is a simple matter to show[5] that with neglect of non-adjacent interaction: three identical atomic orbitals will combine to form bonding, non-bonding and anti-bonding molecular orbitals with energies $Ho + \beta\sqrt{2}$, Ho, and $Ho - \beta\sqrt{2}$, where Ho and β are respectively the Coulomb integral of the constituent atomic orbitals and the resonance integral between two

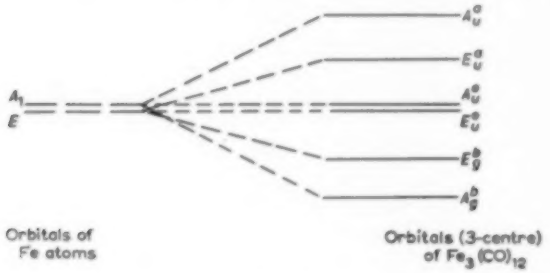


Fig. 1.

adjacent orbitals. Consequently, the three A_1 orbitals interact under the point group D_{3d} of the complete molecule to form $A_{1g}{}^b$ (bonding), $A_{1u}{}^o$ (non-bonding) and $A_{1u}{}^a$ (anti-bonding) three-centre orbitals and similarly the doubly-degenerate orbitals form the corresponding $E_g{}^b$, $E_u{}^o$ and $E_u{}^a$ three-centre orbitals. The relative stabilities of these will depend upon the β and Ho values; although the latter are difficult to evaluate absolutely, it is sufficient to obtain their relative magnitudes.

On account of the trigonal ligand-field the value of Ho for the degenerate orbitals will be decreased slightly with respect to that of the totally symmetric ones; however, this effect will be small as indicated by the following argument. Essentially, ligand-field splitting arises from the electrostatic repulsion of filled orbitals. In the case of an octahedral field, the interaction between the $e_g(3d)$ metal orbitals and ligand σ-orbitals results in the formation of a bonding and anti-bonding orbitals, the latter being largely $3d$ in character and less stable, than the metal $t_{2g}(3d)$ orbitals which are not involved in σ-bonding. It is the separation between these which determines the ligand-field splitting Δ. In our case, however, the A_1 and E orbitals under consideration are those remaining on an iron atom after σ-bonding, consequently, they suffer only a very small splitting due to their different orientations with respect to the σ-bond framework. The resonance integral β between two orbitals can be assumed proportional to both the corresponding overlap integral and the mean ionization potential of the orbitals involved.[6,7] However, since we are considering only the $3d\sigma$ and $3d\pi/3d\delta$ orbitals of iron, for which the ionization potentials are nearly equal, it is justifiable to replace the ratio of β's by that of the overlap integrals (cp. the treatment of metal bis-*cyclo*pentadienyl.[8] The overlap integrals were evaluated for the case $t = 0$, $p = 8$ where these parameters have their usual definition.[9] The value of p was derived on the assumption of a

[5] W. H. EBERHARDT, B. CRAWFORD, JR. and W. N. LIPSCOMB *J. chem. Phys.* **22,** 989 (1954).
[6] R. S. MULLIKEN *J. phys. Chem.* **56,** 295 (1952).
[7] M. WOLFSBERG and L. HELMHOLZ *J. Chem. Phys.* **20,** 837 (1952).
[8] J. D. DUNITZ and L. E. ORGEL *Ibid.* **23,** 954 (1955).
[9] D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL and L. E. SUTTON *J. chem. Soc.* 332 (1954).

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Fe–Fe distance in the above structure similar to that of iron enneacarbonyl and of Slater exponents for the 3*d* atomic orbitals of iron equal to $\alpha_c = 1{\cdot}6$ (calculations of Slater–Condon F_k parameters give further support for this assignment of α-values).* In the case of the *E* orbitals the overlap is of a mixed $d_{\pi\pi}$ and $d_{\delta\delta}$ type, and has a value of about 0·10, whilst that between the A_1 orbitals, of a $d_{\sigma\sigma}$ type, has the value 0·16.†

These results indicate that the orbital splitting ($2\beta\sqrt{2}$) of the totally symmetric orbitals is greater than that of the degenerate orbitals and consequently leads to an order of stabilities as indicated in the molecular-orbital correlation diagram (Fig. 1). This diagram is constructed on the assumption that the ligand-field splitting is less than $\beta_{EE}\sqrt{2}$ an assumption which in view of the above results seems reasonable. We must now accommodate the twelve electrons which remain on the iron atoms after σ-bonding in the above three-centre orbitals. It is obvious that the ground state will possess the configuration $(A_{1g}{}^b)^2(E_{1g}{}^b)^4(E_{1u}{}^a)^4(A_{1u}{}^a)^2$ leading to a diamagnetic molecule.

Acknowledgement—I should like to thank Dr. R. H. GILLETTE, Director of the Institute, for his kind permission to publish this note.

* To be published.

† The overlap integral between two 3*d* orbitals in "end-on" configuration was evaluated before discovery of the result in the appendix of a recent paper.[10] It is gratifying that the formula obtained was identical with that of the above authors.

[10] B. N. FIGGIS and R. L. MARTIN *J. chem. Soc.* 3837 (1956).

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 292 to 294. Pergamon Press Ltd., London

THE SILYL GROUP AS AN ELECTRON ACCEPTOR—II

THE REACTION OF SILYL IODIDE WITH TETRAMETHYLHYDRAZINE

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Abstract—Silyl iodide reacts with tetramethylhydrazine in the gas phase and in solution to yield a 1 : 1 adduct. In the liquid phase, a 2 : 1 compound is also formed. The basic character of tetramethylhydrazine is discussed.

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IN A previous paper,[1] the reaction of silyl iodide, SiH_3I, with hydrazine was described and one of the volatile products was shown to be tetrasilylhydrazine. Vapour-pressure measurements indicated that this new compound had little or no tendency to accept or donate electrons; in particular, no addition compound with silyl iodide was formed, even at low temperatures.

The corresponding carbon compound, tetramethylhydrazine, has been little investigated since it was first prepared in 1953;[2] BELTRAMI and BISSELL[3] showed, however, that it readily reacts with methyl iodide to form a monomethiodide, similar chemically to tetramethylammonium iodide. One of the nitrogen atoms in tetramethylhydrazine therefore donates electrons easily. This conclusion is apparently contradicted by the small value of the basic dissociation constant ($K_b = 2 \times 10^{-8}$) found by CLASS *et al.*,[2] which is even less than that reported for hydrazine itself ($K_b = 8{\cdot}5 \times 10^{-7}$).[4] However, these values were determined in aqueous solution, where solvation effects may be important,[5] and are not directly applicable here. In the absence of hydrogen-bonding solvents, the inductive effect of the methyl group would tend to make tetramethylhydrazine a stronger base than hydrazine.[6]

Tetramethylhydrazine reacted with silyl iodide, both in the gas phase and in dilute solution in dimethyl ether, dibutyl ether, or *n*-hexane, to form a 1 : 1 addition compound. Excess of either reactant could be recovered, leaving a white solid, somewhat soluble in dimethyl ether, but insoluble in dibutyl ether and hexane. In the liquid phase, excess silyl iodide reacted with tetramethylhydrazine to form a 2 : 1 compound, while, with an excess of tetramethylhydrazine, the reacting ratio ($SiH_3I : N_2Me_4$) fell to $<1 : 1$. The results are set out in Table 1.

It seems highly probable that the 1 : 1 compound is similar in structure to the monomethiodide, namely $Me_2NNMe_2{\cdot}SiH_3I$. Alternative structures involving rings or

[1] B. J. AYLETT *J. inorg. nucl. Chem.* **2**, 325 (1956), which becomes Part I of this series.
[2] J. B. CLASS, J. G. ASTON and T. S. OAKWOOD *J. Amer. chem. Soc.* **75**, 2937 (1953).
[3] R. T. BELTRAMI and E. R. BISSELL *J. Amer. chem. Soc.* **78**, 2467 (1956).
[4] G. SCHWARZENBACH *Helv. chim. acta* **19**, 178 (1936).
[5] In the case of methylamines, see:
R. P. BELL and A. F. TROTMAN-DICKENSON *J. chem. Soc.* 1288 (1949).
A. F. TROTMAN-DICKENSON *Ibid*, 1293 (1949).
R. G. PEARSON and F. V. WILLIAMS *J. Amer. chem. Soc.* **76**, 258 (1954).
J. CHATT and G. A. GAMLEN *J. chem. Soc.* 2371 (1956).
[6] H. C. BROWN, H. BARTHOLOMAY and M. D. TAYLOR *J. Amer. chem. Soc.* **66**, 435 (1944).

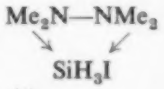
chains, such as 1 or 2, can be excluded because, in the first place, it is known that two vacant orbitals of the silicon atoms are filled only under rather severe conditions.[7]

TABLE 1

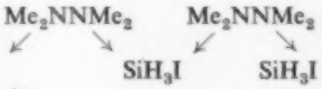
Reaction phase	Reactant in excess	Time of reaction*	SiH_3I: N_2Me_4
Gas	SiH_3I	30 min	1·02:1.
Gas	N_2Me_4	30 min	1·01:1.
Soln. in Me_2O	SiH_3I	10 min	0·82:1.
Soln. in Me_2O	N_2Me_4	30 min/−40°	1·01:1.
Soln. in *n*-Bu_2O	SiH_3I	18 hr	1·08:1.
Soln. in *n*-hexane	SiH_3I	14 hr	0·93:1.
Liquid	SiH_3I	30 min	1·78:1.
Liquid	SiH_3I	3 hr	2·11:1.
Liquid	N_2Me_4	5 min	0·92:1.
Liquid	N_2Me_4	3 hr	0·77:1.

* At room temperature unless otherwise stated.

In addition, there is no evidence that a compound with two adjacent nitrogen atoms can, by



(1)



(2)

donation of electrons, form a chelate compound with a three-membered ring;[8] the disposition of the orbitals concerned makes this most unlikely. The 2 : 1 compound must utilize electrons from both nitrogen atoms, being $IH_3Si{\cdot}Me_2NNMe_2{\cdot}SiH_3I$; in accordance with the poor stability of the di-acid salts of hydrazine,[9] it is formed only when high local concentrations of silyl iodide are present.

EXPERIMENTAL

The vacuum system was of a mercury-free type.[1]. Silyl iodide was prepared by the reaction of silane with hydrogen iodide. Tetramethylhydrazine was prepared by the method of CLASS *et al.*, and purified by fractionation in a micro-column[10] at low temperatures (b.p. −16°/12·5 mm; 72·9/760 mm). Solvents were dried (CaH_2) and fractionated *in vacuo*.

Reaction of silyl iodide with tetramethylhydrazine

(1) *In the gas phase.* The apparatus has been described previously.[1] In a typical experiment, 0·2339 g of silyl iodide (excess) reacted with 0·0494 g of tetramethylhydrazine. Immediately the vapours mixed, a white solid was produced as a fine smoke. This later settled on the walls of the reaction bulb. After 30 min at room temperature, the volatile products were found to be: <0·1 ml

[7] B. J. AYLETT, H. J. EMELÉUS and A. G. MADDOCK *J. inorg. nucl. Chem.* **1**, 187 (1955).
[8] L. F. AUDRIETH and B. A. OGG *The Chemistry of Hydrazine* Chap. 9. Wiley, New York (1951).
[9] H. H. SISLER *Comprehensive Inorganic Chemistry* Vol. V, p. 33. Van Nostrand, Princeton, New Jersey (1956).
[10] B. J. AYLETT *J. chem. Soc.* 4152 (1957).

hydrogen, 0·005 g of monosilane, and 0·1436 g of unused silyl iodide. (Reacting ratio, $SiH_3I : N_2Me_4$, 1·02 : 1). After prolonged pumping, some of the solid product was transferred to the system.

(2) *In solution.* These experiments were carried out in Pyrex tubes of about 100 ml capacity. In a typical one, the reactants were distilled in successively in the order: silyl iodide, dimethyl ether, and tetramethylhydrazine, while the tube was immersed in liquid nitrogen. After the tube had been sealed off, it was allowed to warm to room temperature. As soon as the silyl iodide melted, a white solid formed in the liquid, together with a fine smoke in the upper part of the tube. The smoke later settled on the walls as a fine film; this film could be dissolved in the ether by cautiously shaking the tube. When excess silyl iodide was used in dimethyl ether solution, it was extremely difficult to separate the two after reaction; a similar effect has been noted recently.[11] A sample of the 1 : 1 solid product, after 3 weeks at room temperature *in vacuo*, had decomposed to yield monosilane, hydrogen iodide, and a cream-coloured solid insoluble in ether, acetone, or acetonitrile.

(3) *In the liquid phase.* The two reactants were distilled successively into a small bulb (60 ml) immersed in liquid nitrogen, the bulb was sealed off, and the whole allowed to warm to room temperature. Reaction occurred as soon as the silyl iodide melted, and a greenish-yellow solid was formed. This later often became cream-coloured. In a typical experiment, 0·3923 g of silyl iodide reacted with 0·0830 g of tetramethylhydrazine for 3 hr at room temperature. 0·0780 g of silyl iodide was recovered (reacting ratio 2·11 : 1), together with 1 ml hydrogen and 0·0042 g of monosilane.

[11] H. E. OPITZ, J. S. PEAKE and W. H. NEBERGALL *J. Amer. chem. Soc.* **78**, 292 (1956).

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J. Inorg. Nucl. Chem., 1958, Vol. 5. pp. 295 to 303. Pergamon Press Ltd., London

THE INFRA-RED SPECTRA OF METAL ACETYLACETONATES IN THE SODIUM CHLORIDE REGION

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(*Received* 14 *November* 1956)

Abstract—The infra-red spectra of eighteen metal derivatives of acetylacetone have been studied in the sodium chloride region. The spectra of all the compounds, including those of the alkali metals, are markedly similar in this region, indicating that the arrangement of acetylacetone groups around the metal atom is similar for all of the compounds studied. Structural implications of differences in infra-red absorption frequencies among acetylacetonates are discussed.

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THE nature of the metal–oxygen bonding in metallic derivatives of enols has been the subject of much speculation since the cyclic, chelated structure for these complexes became generally accepted.[1] In recent years several investigators have examined the infra-red spectra of metal derivatives of acetylacetone and other enols[2–7] in the hope of providing some information about the problem of bonding. The most complete and thorough of these infra-red structural studies are those of DUVAL, FREYMANN and LECOMTE[2] who were able to make vibrational assignments for most of the absorption bands of metal acetylacetonates by considering the spectra to be derived from the in-phase and out-of-phase coupled vibrations of two joined acetone molecules. These workers stated that the spectra required a cyclic chelated form for the acetylacetone complexes, but they recognized that their studies did not give conclusive information about the nature of the bonds to the metal atoms.

Since numerous discrepancies are found in published data on the infra-red absorption of metal acetylacetonates, we thought it important to repeat determinations of the spectra in the sodium chloride region for a number of these compounds, using previously analysed samples (Table 1). None of the previous investigators has reported analyses for acetylacetonates used for spectral studies. The absorption bands for the 18 compounds studied are given in Table 2, and some illustrative spectra are shown in detail in Fig. 1.

No infra-red studies on acetylacetonates of univalent metals have been published previously. Six such compounds are included in the present study. Their spectra are of special interest because co-ordinate covalent bonding to the metal should be considerably less important than in the acetylacetonates of polyvalent metals. The

[1] H. DIEHL *Chem. Rev.* **21**, 39 (1937).
[2] J. LECOMTE *Disc. Faraday Soc.* **9**, 125 (1950); C. DUVAL, R. FREYMANN and J. LECOMTE *Bull. soc. chim.* **19**, 106 (1952).
[3] L. J. BELLAMY and R. F. BRANCH *J. Chem. Soc.* 1954, 4491; L. J. BELLAMY, G. S. SPICER and J. D. H. STRICKLAND *J. chem. Soc.* 1952, 4653.
[4] D. M. SHIGORIN *Izv. Akad. Nauk S.S.S.R. Ser. Fiz.* **17**, 196 (1953); *Zh. Fiz. Khim.* **27**, 554 (1953).
[5] R. L. BELFORD, A. E. MARTELL and M. CALVIN *J. inorg. nucl. Chem.* **2**, 11 (1956).
[6] H. W. MORGAN *U.S. Atomic Energy Commission Report* AECD 2659 (1949).
[7] D. JOHNSON Thesis, University of Wisconsin.

large and weakly polarizing ions of the heavy alkali metals are known for their reluctance to act as electron pair acceptors.[8] If chelation implies covalent bonding to the metal atom, then it should be a minimum in the acetylacetonates of these elements.

Unlike acetylacetonates of most divalent and trivalent metals, alkali metal derivatives of beta-diketones are "saltlike" in their physical properties and highly dissociated in dilute solution in ethanol.[9a] The lithium and sodium compounds of this type become more "covalent" in their properties (lower melting and more soluble in hydrocarbons) when the alkali metal ion is complexed by two or more additional donor groups, e.g. water molecules or a molecule of diketone.[9b] Thallium acetylacetonate, however, has "covalent" properties in the absence of additional complexing.[10]

EXPERIMENTAL*

Infra-red spectra. Baird Model S and Perkin–Elmer Model 21 automatic recording double-beam spectrophotometers were used. The infra-red spectrum in the region 625–5000 cm^{-1} of each compound was determined both as a pressed disc in KBr, and as a mull in white petroleum oil. No significant differences were found.

The frequencies given in Table 2 are believed to be correct to ± 8 cm^{-1} in the region 1100–1700 cm^{-1} and to ± 5 cm^{-1} in the region 625–1100 cm^{-1}. Between 1700 and 5000 cm^{-1} the compounds showed no absorbtion except for weak bands at about 2900 cm^{-1} due to C—H stretching. These did not seem to show significant variations, and were not carefully examined in our study.

Analyses. As earlier workers have reported[11] it is difficult to obtain good combustion analyses of alkali metal acetylacetonates. We analysed these compounds volumetrically as follows: a weighed sample was dissolved in water and immediately titrated with HCl to an end point at pH 4·5[12] using a glass electrode pH meter. Accuracy is estimated to be better than ± 1 per cent.

Sodium acetylacetonate. Sodium (0·7 g, 0·03 mole) was dissolved in absolute ethanol (30 ml). To the resulting sodium ethoxide solution was added 3 g (0·03 mole) of acetylacetone (Eastman Kodak white label). Anhydrous ether (50 ml) was added and the mixture was stored at 5°C overnight. The fine white crystals of product which formed were filtered with suction, washed with anhydrous ether, and dried *in vacuo*. Yield 2·5 g (80 per cent).

Lithium acetylacetonate, potassium acetylacetonate, and calcium acetylacetonate were prepared in the same manner as the sodium compound. The lithium compound is highly soluble in ethanol, and in this case the amount of ethanol was reduced to 20 ml and no ether was added.

Caesium acetylacetonate. Caesium amalgam was prepared in low yield by the electrolysis of a concentrated solution of CsCl with a mercury cathode, using a method described for the preparation of barium amalgam.[13] The amalgam was separated and washed twice with small portions of absolute ethanol to remove water, and then shaken

* The symbol A will be used to represent the acetylacetonate group in this and subsequent sections of this paper.

[8] K. FAJANS and G. ZOOS *Z. Physik* **23**, 1 (1924); K. FAJANS *Naturwiss.* **11**, 165 (1923); *Z. Kristallogr.* **61**, 18 (1924).

[9] (a) E. WHITE *J. chem. Soc.* 1929, 1413; (b) N. V. SIDGWICK and F. M. BREWER *Ibid.* 127, 2379 (1925); F. M. BREWER *Ibid.* 1931, 361.

[10] R. C. MENZIES and A. R. P. WALKER *J. chem. Soc.* 1936, 1678

[11] L. F. HATCH and G. SUTHERLAND *J. org. Chem.* **13**, 249 (1948).

[12] L. G. VAN UITERT, C. G. HAAS, W. C. FERNELIUS and B. E. DOUGLAS *J. Amer. chem. Soc.* **75**, 455 (1953).

[13] B. C. MARKLEIN, D. H. WEST and L. F. AUDRIETH *Inorg. Synth.* **1**, 12 (1939).

vigorously with a third portion of ethanol to give a solution of caesium ethoxide. Acetylacetone was then added dropwise to the solution until a test drop gave a neutral reaction in water. White crystals of the caesium compound[14] were precipitated.

Thallium acetylacetonate. Finely-divided thallium metal (2·0 g, 0·01 mole) was dissolved in warm ethanol with the aid of oxygen. Acetylacetone (1·0 g, 0·01 mole) was added to the warm solution, which was then chilled. The white crystals of TlA which formed were filtered off, washed with ethanol and recrystallized from chloroform. Yield 2·0 g (65 per cent); m.p. 158–159°, lit. 160·5°.[10]

Silver acetylacetonate. This compound was prepared by mixing equimolar quantities of approximately one M solutions of $AgNO_3$ and $C_5H_7O_2Na$ dissolved in oxygen-free water. The creamy-white silver compound precipitated immediately. It was filtered rapidly onto a porous sintered glass plate and quickly washed with a little oxgen-free water, then dried under high vacuum. The yield is nearly quantitative. The compound was analysed by treating with excess standard NaCl solution, followed by titration of excess chloride with $AgNO_3$.

Silver acetylacetonate, first prepared in 1893,[15] has not been well characterized. The pure compound can be kept for a few days with only moderate darkening.

TABLE 1.—ANALYTICAL DATA

Compound	Method of prep.	Calculated			Found		
		C	H	Equiv. wt.	C	H	Equiv. wt.
CsA	†			232			234
KA	†			138			139
NaA	†			122			121
LiA	†			106			106
TlA	†*	19·8	2·32		20·0	2·34	
AgA	†			207			207
CaA_2	†			119			119
MgA_2	(16)	54·0	6·3		54·4	6·4	
BeA_2	(16)*	58·0	6·8		58·3	6·9	
CoA_2	(17)	46·7	5·5		46·3	5·3	
CuA_2	(18)*	45·9	5·4		45·7	5·6	
ZnA_2	(16)*	45·6	5·4		45·6	5·3	
PdA_2	(‡)*	39·4	4·6		39·1	4·9	
LaA_3	(19)	40·4	4·7	145	39·9	4·6	146
AlA_3	(17*a*)*	55·7	6·5		56·1	6·4	
FeA_3	(19)	51·0	6·0		51·3	6·1	
CrA_3	(20)	51·6	6·1		51·8	5·8	
CoA_3	(20)	50·6	5·9		50·6	5·9	

* Purified by sublimation *in vacuo*. † See experimental section.
‡ Prepared by the reaction of acetylacetone with a solution of $PdCl_2$.

[14] G. T. MORGAN and H. W. MOSS *J. chem. Soc.* 105, 189 (1914).
[15] J. U. NEF *Ann. Chem.* **277**, 68 (1893).
[16] A. ARCH and R. C. YOUNG *Inorg. Synth.* **2**, 17 (1945).
[17] F. GACH *Monatsh. Chem.* **21**, 100 (1900).
[17a] R. C. YOUNG *Inorg. Synth.* **2**, 25 (1946).
[18] A. COMBES *C.R. Acad. Sci., Paris.* **119**, 1122 (1894).
[19] A. HANTZSCH and C. H. DESCH *Ann. Chem.* **323**, 1 (1902).
[20] B. E. BRYANT and W. C. FERNELIUS *Inorg. Synth.* **5**, in press.

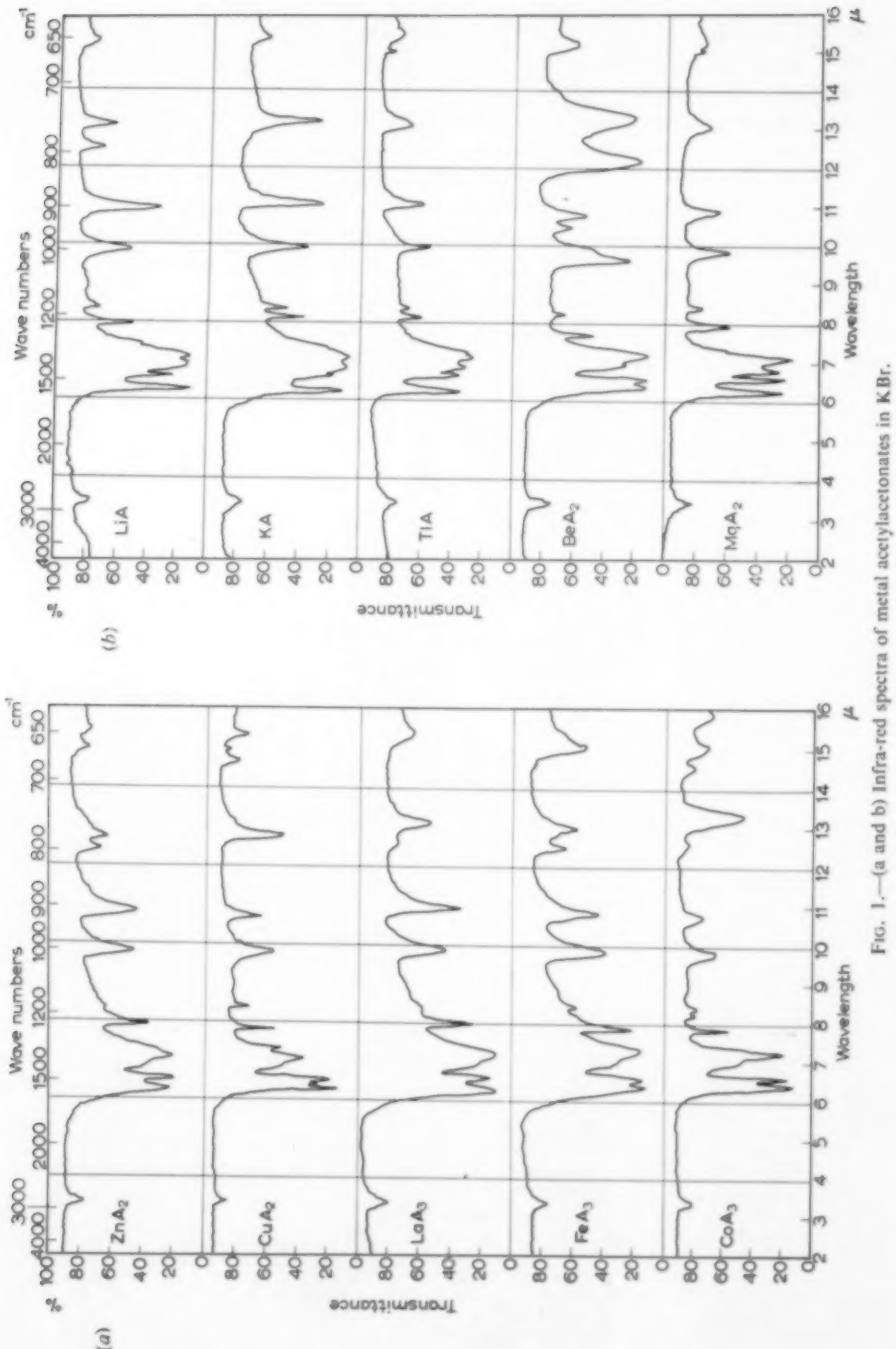

FIG. 1.—(a and b) Infra-red spectra of metal acetylacetonates in KBr.

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Decomposition with the liberation of silver is more rapid when the compound is exposed to water, organic solvents, or oxygen, or when it is heated. AgA is insoluble in and not wetted by water, slightly soluble in ethanol, and insoluble in benzene, ether and chloroform.

Other acetylacetonates were prepared by standard methods referred to in Table 1. The compounds were purified by recrystallization, followed by drying or sublimation *in vacuo*.

RESULTS

The frequencies found for BeA_2, ZnA_2, CoA_2, AlA_3, FeA_3, CrA_3 and CoA_3 are in fairly good general agreement with those reported by LECOMTE,[2] while those for CuA_2 agree well with those found by CALVIN.[5]

From an examination of the frequencies listed in Table 2, or the spectra shown in Fig. 1, it is apparent that the general appearance of the spectrum and position of absorption bands is strikingly similar for all of the acetylacetonates. The physical

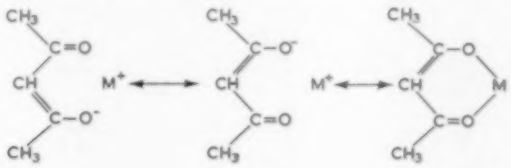

FIG. 2.

properties of the compounds cannot be correlated with their infra-red spectra. For instance, the highly saltlike compound CsA has a spectrum virtually identical with that of the "covalent" TlA. Likewise, the inner orbital[21] complex CoA_3[22] has a spectrum closely similar to that of the outer orbital complex FeA_3.[23] The differences between the spectra among the compounds studied appear to be differences of degree rather than of kind. LECOMTE noticed the similarity among spectra of covalent acetylacetonates and stated that "the main regions of absorption for all of the acetylacetonates are found in the same position, whatever the metal."[20] We confirm this generalization and find that it holds true even for the highly ionic alkali metal compounds.

The close similarity of the spectra of the alkali metal acetylacetonates to those of the polyvalent acetylacetonates is evidence that the geometrical arrangement of acetylacetonate groups around the metal atoms must be much the same for both types of compounds. Both the infra-red spectra and the other properties of the alkali metal compounds are consistent with an essentially ionic structure, with the oxygen atoms of the symmetrical enolate anions taking up positions near to the metal ions in the crystals (Fig. 2a and b). The number of oxygens which are "nearest neighbours" equidistant from each alkali metal ion is probably greater than two, accounting for the high melting point and "ionic" solubility behaviour of these compounds.

In considering differences between positions of absorption bands among acetylacetonates, most attention has been paid to the prominent band at 1560–1620 cm^{-1}.

[21] H. TAUBE *Chem. Rev.* **50**, 69 (1952).
[22] L. CAMBI and L. SZEGO *Ber. dtsch. chem. Ges.* **64**, 2591 (1931).
[23] R. O. WHIPPLE, R. WEST and K. EMERSON *J. chem. Soc.* 1953, 3715.

TABLE 2.—INFRA-RED ABSORPTION FREQUENCIES IN CM^{-1}

CsA	KA	NaA	LiA	TlA	AgA	CaA_2	MgA_2	BeA_2	CoA_2	CuA_2	ZnA_2	PdA_2	LaA_3	AlA_3	FeA_3	CrA_3	CoA_3
1613	1608	1604	1595	1610	1612	1607	1608	1572	1592	1572	1588	1561	1610	1586	1570	1568	1565
										1553		1543					
1506	1508	1508	1512	1507	1508	1508	1520	1529	1517	1527	1524	1520	1514	1527	1525	1522	1520
1464	1456	1462	1443	1464	1464	(1462)	1474	1444	1464	(1455)	(1454)		(1439)	(1466)	(1428)	1424	(1429)
1408	1408	1408	1404	1412	1414	1395	1409	1393	1402	1408	1404	1393	1385	1389	1368	1383	1385
	(1383)	(1360)	(1346)	(1385)	(1366)	(1362)	(1367)		(1368)	(1360)	(1371)	(1357)	(1360)	(1364)		(1364)	(1365)
1230	1232	1228	1258	1230	1232	1244	1262	1300	1258	1274	1261	1267	1252	1285	1272	1279	1279
																	(1216)
(1199)	(1197)	(1193)	(1195)	(1198)		(1200)	(1193)	(1215)	(1196)	(1190)	(1195)	(1195)	(1190)	1188	1188	1190	(1190)
1009	1009	1008	1014	1008	1008	1013	1018	1040	1016	1018	1017	1018	1010	1026	1015	1019	1022
							(937)	(1013)									
								(957)									
909	905	906	915	905	905	915	920	921	919	933	922	930	917	931	923	928	932
			800				(783)	822	(789)		804	784	(792)	(790)	(800)	(793)	(792)
763	760	763	763	765	764	778	768	753	766	781	786	778	762	763	769	770	752
												696					
						(720)				680		674		682	(722)	683	688
658	652	650	654	646		651	656	660	649	650	645	658	647	657	663	656	663

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This band is one of two which LECOMTE assigns to the C=O stretching vibration.[2] Among acetylacetonates of six divalent metals, BELLAMY found little difference in the position of this carbonyl peak.[3] We find slight but apparently real differences in the position of the first carbonyl band among such complexes. The carbonyl band is shifted to lower frequency in spectra of the acetylacetonates of the more electronegative metals. A shift in this direction implies a loosening of the C–O bond, probably as a result of increased covalent metal–oxygen bonding in the compounds containing the more negative metals.* Among the acetylacetonates of divalent metals, there is a roughly linear relationship between carbonyl frequency and second ionization potential of the metal (Fig. 3),† and hence also between frequency and stability of the complex.[24]

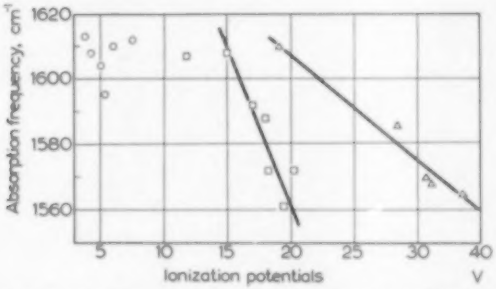

FIG. 3.—Position of the first carbonyl band vs. ionization potential.
○ univalent metals, first ionization potentials;
□ divalent metals, second i.p.;
△ trivalent metals, third i.p.;
All ionization potentials from W. FINKELSTEIN and W. HUMBACH *Naturwiss.* **42**, 35 (1955).

In so far as we can judge from the few examples which were studied, a similar relationship also holds for the trivalent metals, but not for the univalent metals. Among the latter, more ionic complexes, there is no correlation between first ionization potential and frequency of the first carbonyl band. There is a small shift toward lower frequency for NaA and especially LiA, perhaps a result of polarization effects due to the small size of the lithium and sodium ions.

The second carbonyl band, at 1360–1415 cm^{-1}, shows a somewhat more irregular variation with ionization potential. However, in general, this band shifts in the opposite direction to the first carbonyl band; that is, to higher frequency with increasing ionization potential. Other absorption bands also show irregular frequency shifts, but, in general, for bands other than the carbonyl bands, mass (or ion size) effects seem to be more important than ionization potential; the largest shifts are usually found for LiA and BeA_2.

LECOMTE[2] found bands in the 600–700 cm^{-1} region which varied depending on the nature of the metal, and which he tentatively ascribed to metal–oxygen vibration. We find slight variations in the positions of absorption bands in the 650 cm^{-1} region, but far less variation, and also lower intensity, than would be expected for bands due to

* A similar relationship between carbonyl frequencies and ionization potential was noted by BELLAMY[3] among metal derivatives of salicyladehyde.

† The point for the highly ionic CaA_2 appears on the plot, but was not used in determining the position of the line.

[24] L. G. VAN UITERT, W. C. FERNELIUS and B. E. DOUGLAS *J. Amer. chem. Soc.* **75**, 2736 (1953).

metal–oxygen vibration. In our opinion, for most acetylacetonates, bands due to metal–oxygen vibration should be found out of the sodium chloride region, at less than 600 cm^{-1}. The first-row metals may be exceptions to this generalization, because their very low mass should lead to a high vibrational frequency. An example is beryllium, which shows a *very strong* band at 822 cm^{-1}, in a region where none of the other compounds show marked absorption. A similarly intense band at nearly the same frequency is also found in the infra-red spectrum of beryllium basic acetate, $Be_4O(CH_3COO)_6$. Tentatively we assign this band to the Be—O stretching vibration.

FIG. 4.

FIG. 5.

Finally, we should like to put forth some speculations regarding bonding in metal acetylacetonates. The metal acetylacetonates are commonly supposed to have symmetrical, resonance-stabilized structures. The most important evidence leading to this belief is the work of CALVIN and WILSON[25] who have shown convincingly that resonance in the enol ligand is much more important for the stability constant of the Cu(II) complex than it is for the acid dissociation constant of the enol, i.e. that enol resonance is much more important for the copper than for the hydrogen compound. To explain this, CALVIN proposed two structures, both involving resonance in a chelate ring covalently bonded to copper (Figs. 4 and 5). However, both of CALVIN's models require that the copper be symmetrical with respect to the two oxygens of the ring in order for resonance to take place. Recent X-ray structure determinations for CuA_2 show that the C—O and O—Cu distances for each oxygen of the acetylacetonate ligand are slightly but significantly different.[26,27,28]*

It is our suggestion that CALVIN's results can be explained on the basis of a model involving resonance between the ionic and covalent forms, with an appreciable contribution of the ionic form to the resonance hybrid. This ionic-covalent resonance model (Fig. 2) does not require symmetrical placement of the copper atom, and is

* Cf. bond distances in the closely related copper(II) tropolonate.[28]

[25] M. CALVIN and K. W. WILSON *J. Amer. chem. Soc.* **67**, 2003 (1947).
[26] E. A. SHUGAM *Dokl. Akad. Nauk. S.S.S.R.* **81**, 853 (1951). Cu—O 1·94 and 1·88 Å; C—O 1·25 and 1·30 Å.
[27] H. KOYAMA, Y. SAITO and H. KUROYA *J. Inst. Polytech. Osaka City Univ., Ser. C* **4**, 43 (1953). C—O 1·94 and 1·95 Å; C—O 1·24 and 1·29 Å.
[28] J. M. ROBERTSON *J. chem. Soc.* 1951, 1222.

therefore more consistent with the known structure of CuA_2.* CALVIN's stability data[25] is explained by our model, if we assume that the ionic form makes a significantly greater contribution to the resonance hybrid in CuA_2 than in HA. With metals more electropositive than copper, the relative importance of the ionic form should be still greater,[32]† and the structure should become more nearly symmetrical.[33]‡

(*Note added in proof*) HOLTZCLAW and COLLMAN[34] have recently published a paper on infra-red absorption of metal chelates of various beta-diketones. These authors, studying acetylacetonates of seven divalent metals and of sodium, find a relationship between the frequency of the carbonyl absorption and the stability constant for the complex. This finding is confirmed by our work.

* According to Pauling's postulate of $3d4s4p^2$ bonding in planar Cu(II) complexes,[29] one might not at first sight expect an important contribution from the ionic form, because the Cu^{++} ion could only be present as an excited state with a $3d$ electron "promoted" to the $4p$ level. Actually, our model is not inconsistent with $3d4s4p^2$ hybridization about copper, since the ionic excited state should be strongly stabilized by crystal field forces.[30] In addition, our structure is thoroughly consistent with HUGGINS' suggestion of $4s4p^34d$ bonding to Cu(II) in planar copper complexes.[31]

† While there is no direct evidence to this point, it is known that the influence of the acid dissociation constants of diketones on the stability of their metal complexes decreases in the order Cu Ni Ba.[32]

‡ Significant differences in C—O and Fe—O distances were not found in FeA_3.[33]

[29] L. PAULING, *The Nature of the Chemical Bond*, p.104, Second Edition, Cornell Univ. Press, Ithaca, New York, 1945.
[30] L. E. ORGEL *J. chem. Soc.* 1952, 4756.
[31] M. HUGGINS *J. chem. Phys.* **5**, 527 (1937); cf. D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL and L. E. SUTTON *J. chem. Soc.* 1954, 332.
[32] L. G. VAN UITERT, W. C. FERNELIUS and B. E. DOUGLAS *J. Amer. chem. Soc.* **75**, 457 (1953).
[33] R. B. ROOF, JR. *Acta. Cryst.* **9**, 781 (1956).
[34] H. F. HOLTZCLAW, JR. and JAMES P. COLLMAN *J. Amer. chem. Soc.* **79**, 3318 (1957).

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 304 to 307. Pergamon Press Ltd., London

THE SYNTHESIS OF BROMOPENTAMMINEOSMIUM(III) HALIDES*

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Abstract—Certain observations relative to DWYER and HOGARTH's methods for the synthesis of bromopentammineosmium(III) and hexammineosmium(III) salts are recorded here together with hitherto unreported physical properties of specific compounds of the former type.

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BY analogy,[1] compounds of the type indicated above are of particular interest as starting materials for the formation of compounds of osmium in the zero oxidation state. Accordingly, we have repeated the experiments of DWYER and HOGARTH[2, 3] for the synthesis of salts of the bromopentammineosmium(III) and hexammineosmium(III) ions. Since our findings in the latter case differ in some respects from those reported by DWYER and HOGARTH, and because our investigations extend beyond their efforts, it seems worthwhile to record the results of our experiments.

This brief report serves to record the details of methods and procedures employed also in other studies to be described in forthcoming publications from this laboratory.

EXPERIMENTAL

Materials

With the exceptions noted below, all materials used in this work were reagent grade chemicals that were used without further treatment.

Ammonia hexabromoösmate(IV) was prepared in 95–98 per cent yields by the method of DWYER and GIBSON.[4, 5] (Found: Os, 27·0; Br, 67·9; N, 4·00. Calc. for $(NH_4)_2OsBr_6$: Os, 26·95; Br, 67·97; N, 3·97%). The measured paramagnetic moment of the central Os^{4+} (1·55 B.M.) is to be compared with 1·51 B.M. reported elsewhere.[6] This product gave an X-ray diffraction pattern that yielded data in good agreement with those previously reported.[7]

Methods

Analytical. Osmium was weighed as the metal following reduction with ammonia[2, 4] or hydrogen[8] at 450–550°. In most cases, bromine was determined *in tandem* using a procedure similar to that employed by LARSON and GARNER.[9] Otherwise, standard analytical methods were used.

* This work was supported, in part, by the U.S. Atomic Energy Commission, Contract AT-(40-1)-1639.
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[1] G. W. WATT and P. I. MAYFIELD *J. Amer. chem. Soc.* **75**, 6178 (1953).
[2] F. P. DWYER and J. W. HOGARTH *J. roy. Soc. N.S.W.* **84**, 117 (1951).
[3] F. P. DWYER and J. W. HOGARTH *Ibid.* **85**, 113 (1952).
[4] F. P. DWYER and N. A. GIBSON *Nature, Lond.* **165**, 1012 (1950).
[5] F. P. DWYER Private communication.
[6] R. B. JOHANNESEN and A. R. LINDBERG *J. Amer. chem. Soc.* **76**, 5349 (1954).
[7] U.S. nat. Bur. Stand. circ. 539, vol. III, 71 (1953).
[8] R. GILCHRIST *J. Res. nat. Bur. Stand.* **6**, 421 (1931).
[9] L. L. LARSON and C. S. GARNER *J. Amer. chem. Soc.* **76**, 2180 (1954).

Reactions with gaseous ammonia at elevated temperatures. These reactions were carried out in a small stainless steel autoclave (12·8 × 7·6 cm., i.d.) fitted with a needle valve, pressure gauge, and thermometer well, and heated with an electric furnace.

X-ray diffraction. Powder patterns were obtained with a Hayes X-ray spectrograph using Cu$K\alpha_1$ radiation, a nickel filter, a tube voltage of 30 kV and a filament current of 10–15 mA. The instrument was equipped with both a 14-cm camera and a recording diffractometer; when the former was used, exposure times varied from 5 to 11 hr, and the powdered samples were diluted with starch in ratios of 1 : 5 to 1 : 10 and sealed in capillaries made of X-ray glass of 0·1 to 0·33 mm o.d. and a wall thickness of 0·01 mm.[10]

Magnetic susceptibility measurements. Magnetic moments were determined with a Curie–Cheneveau type torsion balance constructed essentially as described by GRAY and FARQUHARSON;[11] however, a permanent magnet was used and its motion was controlled by a reversible electric motor. Measurements were made using solid substances and the reliability of the instrument was established by measuring the paramagnetic susceptibilities of several common complex compounds of transitional metals with known magnetic moments. The balance was calibrated at frequent intervals using nickel(II) chloride solution.[12] Unless indicated to the contrary, the paramagnetic moments reported in this and subsequent papers in this series relate to the compound rather than to the central paramagnetic atom or ion, i.e. corrections for diamagnetic constituents were not made.

Synthesis of bromopentammineosmium(III) bromide 1-hydrate

Ammonium hexabromoösmate(IV) (0·5 g) contained in a platinum crucible was treated exactly as described by DWYER and HOGARTH.[2] The yield of the resulting fawn-coloured microcrystalline powder was only 0·036 g, or 10 per cent, which apparently is consistent with experiences with this method in Professor DWYER's laboratory.[5] (Found: Os, 35·90; Br, 45·05. Calc. for $[Os(NH_3)_5Br]Br_2 \cdot H_2O$: Os, 35·68; Br, 45·03%). X-ray diffraction data for this compound are given in Table 1.

Synthesis of bromopentammineosmium(III) iodide

This previously reported[2] substance was obtained in the course of an attempt to prepare hexammineosmium(III) iodide. Thus, 0·27 g of $(NH_4)_2OsBr_6$ was treated as described by DWYER and HOGARTH.[3] The initial solid reaction product was leached with water and solid sodium iodide was added to the clear water extract; thereupon, a pale yellow precipitate formed in a quantity too small to permit analysis. This precipitate was removed by filtration and solid ammonium sulphate was added to the filtrate. There was no immediate change, but when the solution was cooled to 0° we obtained a small quantity of a yellow precipitate that proved to be $[Os(NH_3)_5Br]I_2$ rather than the $[Os(NH_3)_6]I(SO_4)$ reported by DWYER and HOGARTH. This product was separated by filtration, washed with 95 per cent alcohol, and dried over magnesium perchlorate. (Found: Os, 31·90; N, 11·80; $\mu = 1{\cdot}6$ B.M. Calc. for $[Os(NH_3)_5Br]I_2$: Os, 31·23; N, 11·50%). X-ray diffraction data are included in Table 1.

[10] *Glaskapillaren für röntgenographische Aufnahmen nach Debye–Scherrer*, Walter Gleichmann, *Glas- u. Quarzglasbläserei*, Berlin-Heiligensee.
[11] F. W. GRAY and J. FARQUHARSON *J. sci. Instrum.* **9**, 1 (1932).
[12] H. R. NETTLETON and S. SUGDEN *Proc. roy. Soc.* **A 173**, 313 (1939).

TABLE 1.—X-RAY DIFFRACTION DATA

$[Os(NH_3)_5Br]Br_2 \cdot H_2O$		$[Os(NH_3)_5Br]Br_2$				$[Os(NH_3)_5Br]I_2$	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
5·82	1·00	5·85	1·00	2·75	0·50	6·2	1·00
4·25	0·20	4·29	0·20	2·68	0·20	4·52	0·20
3·80	0·20	3·84	1·00	2·13	0·20	4·33	0·20
3·42	0·30	3·45	0·50	1·92	0·20	3·86	0·60
3·21	0·20	3·21	0·20	1·74	0·20	3·67	0·40
2·71	0·50					2·83	0·30

Synthesis of bromopentammineosmium(III) bromide

In the preceding experiment, only a minor portion of the initial solid reaction product dissolved in water. Accordingly, the solid residue was repeatedly leached with water and each such extract was treated with a few drops of 48 per cent HBr, ethanol was then added, and the resulting mixture was cooled to 0°. In this manner we obtained several fractions of solid crystalline materials that were fractionated further in the manner described above until the quantities of product remaining were sufficient only for analysis. In order of increasing solubility in water, the osmium content decreased from 39·7 to 37·0 per cent, while the bromine content increased from 43·3 to 46·6 per cent, i.e. the Os : Br ratio increased from 1 : 2·59 to 1 : 3·01. Correspondingly, the intensity of colour of these products decreased progressively from yellow-tan to cream-coloured, and the magnetic susceptibility per g of substance ($\chi_g \times 10^6$) increased from 1·3 to 3·6. The least soluble fraction (not analysed) was diamagnetic. The analytical data corresponding to the most soluble fraction were as follows. (Found: Os, 37·0; Br, 46·6; N, 13·3. Calc. for $[Os(NH_3)_5Br]Br_2$: Os, 36·92; Br, 46·54; N, 13·60%.) On the basis of the formula indicated, $\mu = 2{\cdot}1$ B.M. X-ray diffraction data are included in Table 1.

DISCUSSION

The results described above confirm DWYER and HOGARTH's method for the synthesis of bromopentammineosmium(III) bromide 1-hydrate. However, the procedure by which they obtained hexammineosmium(III) iodide sulphate yielded a small water-soluble fraction from which only bromopentammineosmium(III) iodide was isolated. Fractionation of the major and less soluble product (which apparently was not examined by DWYER and HOGARTH) led to the isolation of the *anhydrous* salt, $[Os(NH_3)_5Br]Br_2$. The data obtained in the course of these latter experiments indicate a progressive separation from an as yet unidentified diamagnetic impurity. DWYER and HOGARTH report that they obtained the hexammine in 50 per cent yield and that the hexammine is more soluble in water than the bromopentammine compound. Accordingly, if the hexammine was formed at all in our experiments, it was eliminated during the fractionation that yielded the anhydrous bromopentammine bromide.

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It is not our intent to imply that the results reported by DWYER and HOGARTH are in error. Rather, it is believed that the differences observed are attributable to procedural variables the nature of which is not at once apparent.

Alternative methods for the synthesis of compounds of the type $[Os(NH_3)_5X]X_2$ and $[Os(NH_3)_6]X_3$ have arisen from our work on the interaction of hexabromo-osmates and liquid ammonia. These results will be included in future papers.

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THE INTERACTION OF AMMONIUM AND POTASSIUM HEXABROMOÖSMATE(IV) AND LIQUID AMMONIA AT 25°—I.

THE AMMONIA-INSOLUBLE PRODUCT*

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Abstract—The ammonia-insoluble product of the interaction of ammonium or potassium hexabromoösmate(IV) and liquid ammonia at or near room temperature is shown to be the hitherto unreported hexammineosmium(III) hexabromoösmate(III). This salt reacts slowly with hydrobromic acid to form hexammineosmium(III) bromide and the acid H_2OsBr_6; the latter was oxidized to H_2OsBr_6 which was isolated as the ammonium salt. Hexammineosmium(III) hexabromoösmate(III) reacts with silver ion to form hexammineosmium(III) ion, impure silver(I) hexabroösmate(III), and other products.

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IN THE course of a search for osmium compounds suitable as starting materials for reduction reactions in liquid ammonia that might lead to compounds of osmium in the zero oxidation state (i.e. similar to those previously observed for iridium[1] and platinum[2]), we have studied a number of osmium compounds initially with respect to their solubility in and reactions with liquid ammonia. Both potassium and ammonium hexabromoösmate(IV) were of interest because of their ease of preparation in high yield and high purity and because of their apparently high solubility in ammonia at −33·5°. It soon became apparent, however, that both of these salts undergo slow reaction with the solvent at −33·5° and considerably more rapid reaction at elevated temperatures.

This is the first in a series of papers concerned with the separation and characterization of the products of these quite complex reactions. Not only did the initial reactions lead to unanticipated products, but the detailed study of these substances has also led to certain hitherto unreported osmium complexes and to improved methods for the synthesis of others.

EXPERIMENTAL

With the exceptions noted below, all materials, methods, and experimental procedures were the same as those described earlier.[3]

Potassium hexabromoösmate(IV) was prepared in 95 per cent yield by a method analogous to that previously described[3] for the corresponding ammonium salt, but modified in a manner suggested by Prof. DWYER.[4] This modification consisted of allowing the solution of OsO_4 in 48 per cent HBr to age for a few days and heating it to boiling before adding potassium bromide and cooling to 0°. The best results were

* This work was supported, in part, by the U.S. Atomic Energy Commission, Contract AT-(40-1)-1639.
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[1] G. W. WATT and P. I. MAYFIELD *J. Amer. chem. Soc.* **75**, 6178 (1953).
[2] G. W. WATT, M. T. WALLING, JR. and P. I. MAYFIELD *Ibid.* **75**, 6175 (1953).
[3] G. W. WATT and L. VASKA *J. inorg. nucl. Chem.*
[4] F. P. DWYER Private communication.

obtained by adding an equivalent quantity of solid KBr rather than an excess of saturated solution. The K_2OsBr_6 product was analysed by reducing with hydrogen[3] and weighing the resulting osmium metal and potassium bromide together; bromine was determined independently (Found: Os + 2KBr, 57·6; Br, 64·7. Calc. for K_2OsBr_6: Os + 2KBr, 57·3; Br, 64·1%). X-ray diffraction data for this salt are given in Table 1.

For the analysis of substances containing osmium, silver, and bromine, such as mixtures of Ag_3OsBr_6 and AgBr, the three elements were determined on a single sample by reducing with hydrogen at 450–550°. The HBr was collected and bromide ion was precipitated and weighed as AgBr. Elemental osmium and silver were weighed together, the osmium was volatilized as OsO_4 by heating in air at 600–700°, the residual silver was weighed directly and osmium was determined by difference. Use of ammonia gas in the reaction was found to be unreliable owing to incomplete reduction of the AgBr. In independent experiments employing pure AgBr, the incomplete reduction with NH_3 at 500–550° and quantitative reduction with hydrogen at 450–550° was verified.

Reactions in liquid ammonia at or near room temperature were carried out, using procedures described elsewhere,[5] except that the Pyrex reaction tubes placed in the autoclave were not sealed.

Qualitative behaviour of ammonium and potassium Hexabromoösmate(IV) toward anhydrous ammonia

As evidenced by colour changes, both the potassium and ammonium salts apparently form ammoniates upon contact with anhydrous ammonia gas. These ammoniates dissolve readily in anhydrous liquid ammonia at −75° to form solutions having a red-brown colour so intense that they are opaque even at low concentrations. Interactions with the solvent that are more profound than simple ammoniation appear to occur only very slowly at −75°. Rate of solution, solubility, and rate of reaction with the solvent are significantly greater at −33·5°, and still greater at or above room temperature. At room temperature, neither the rate of reaction of ammonium hexabromoösmate(IV) with liquid ammonia nor the nature of the reaction products is influenced greatly by the presence of excess ammonium ion added as ammonium bromide; i.e. the reactions are apparently not subject to acid catalysis. However, examination of the data from a considerable number of reactions carried out under different conditions of ammonium ion concentration indicates that the presence of ammonium ion tends to suppress ammonolysis of the ammonia-insoluble product by decreasing the amide ion concentration. Also, there is evidence that the ammonium salt may react metathetically with the ammonia-insoluble product in a manner entirely analogous to that described below for the interaction of the latter with aqueous hydrobromic acid; this reaction in ammonia is quite slow at room temperature but considerably more rapid at 90°. At any of the temperatures indicated above, the solubility of the ammonium salt is somewhat less that that of the potassium salt.

Reactions of ammonium and potassium hexabromoösmate(IV) with liquid ammonia at 23–43°

In an experiment that yielded a reasonably pure ammonia-insoluble product, 5·11 g (7·24 mmole) of $(NH_4)_2OsBr_6$ and 40 ml of anhydrous liquid ammonia were

[5] G. W. Watt and R. G. Post *Industr. Engng. Chem.* **45**, 846 (1953).

allowed to remain in contact for 15 hr at 30° and 12 atm. The products consisted of an amber crystalline solid and an intensely brown-coloured supernatent ammonia solution. After filtration, the amber solid was washed six times with 35 ml portions of liquid ammonia; the first wash solution was yellow, the subsequent one colourless. The solvent was evaporated from the combined filtrate and washings to provide a mixture of yellow-tan and white crystals.* After removal of residual ammonia at 10^{-3} mm, the ammonia-insoluble product was dried over anhydrous magnesium perchlorate (Found: Os, 39·8; Br, 49·5; N, 9·2; μ, 1·74 B.M. based on $[Os(NH_3)_6](OsBr_6)/2$. Calc. for $Os(NH_3)_6](OsBr_6)$: [Os, 39·5; Br, 49·8; N, 8·7)%. The yield was 46 per cent based on $(NH_4)OsBr_6$ used in the reaction.

Essentially the same observations were made when K_2OsBr_6 was used, except that the ammonia-insoluble product exhibited a brown rather than an amber colour. Using both the ammonium and potassium salts, runs were made in which the initial concentration of hexabromoösmate(IV) ion was varied from 0·04 to 0·18 mole/l., the initial concentration of ammonium ion from 0 to 0·80 mole/l, [i.e. calculated as the maximum concentration from added NH_4Br and/or $(NH_4)_2OsBr_6$], the reaction time from 13 to 48 hr, and the temperature from 23 to 43°; the corresponding ammonia pressures ranged from 9 to 16 atm. For the corresponding ammonia-insoluble products, the osmium content ranged from 39·8 to 42·1 per cent and the bromine content from 47·2 to 49·5 per cent, i.e. practically all of these products were of a composition corresponding rather closely to hexammineosmium(III) hexabromoösmate(III). The yields of this product, based on osmium used as bromoösmate(IV) ranged from 46 to 51 per cent. This substance is substantially insoluble in all common organic solvents, including N,N-dimethylformamide and γ-butyrolactone, and at room temperature is insoluble in and unreactive toward water,† 0·02 *N* sodium hydroxide, 0·1 *N* hydrobromic acid, dilute nitric and sulphuric acids, 0·8 *M* sodium bromate, and 5 per cent ammonium nitrate. The amber solid is only slowly attacked by concentrated sulphuric acid, is decomposed readily by concentrated nitric acid with liberation of osmium tetroxide, and reacts with 40 per cent potassium hydroxide with liberation of ammonia and the formation of a brown precipitate. Although the amber solid is unreactive toward liquid ammonia over the range −75 to −33·5° for periods up to 24 hr, reactions that were not investigated in detail occur at higher temperatures.

Reactions of hexammineosmium(III) hexabromoösmate(III) with hydrobromic acid

Treatment of the ammonia-insoluble product with hydrobromic acid served to effect purification by removing relatively small quantities of acid-soluble osmium complexes that were present as impurities in most of the reaction products studied. Of more importance, however, is the fact that identification of products of the reaction between hydrobromic acid and the ammonia-insoluble product provides direct support for the conclusion that the latter is indeed hexammineosmium(III) hexabromoösmate(III).

In a typical experiment, 0·5064 g of the amber solid was treated with 25 ml of 48 per cent HBr for several days at 25°. The acid-insoluble solid was separated from the *red solution* (see below), washed with water, with ethanol, and dried under reduced

* The nature of these products will be described in a later paper.
† Very slow hydrolysis apparently occurs upon contact for several days.

pressure over magnesium perchlorate. The yield was 0·2842 g or 56 per cent (Found: Os, 39·8; Br, 49·8; N, 8·8; μ, 1·76 B.M. Calc. for $[Os(NH_3)_6](OsBr_6)$: Os, 39·5; Br, 49·8; N, 8·7%.) X-ray diffraction data, which were substantially identical with those for the original ammonia-insoluble product, are included in Table 1.

Similar reactions with hydrobromic acid were studied at several temperatures (25–90°) and times of contact (4 hr to 13 days). At 25° the amber solid appeared to be essentially unreactive toward hydrobromic acid over periods of several hours. At higher temperatures and over longer periods of contact, however, both the extent of reaction and the purity of the acid-insoluble product increased. In this manner, all of the ammonia-insoluble products were purified, with yields of the resulting $[Os(NH_3)_6](OsBr_6)$ as high as 97 per cent.

The red solution from the preceding separation was evaporated at 60°, small portions of ethanol were added as the evaporation progressed, and orange-coloured crystals began to separate. When the solution volume was reduced to 10 ml, 40 ml of ethanol was added, and the resulting solution was cooled at 0° for 1 day. The crystals were removed from the red solution by filtration, washed with ethanol, and dried *in vacuo*. This solid was recrystallized twice by dissolving it in a minimum volume of water at 25°, and diluting the solution five-fold with a saturated solution of ammonium bromide in ethanol. The product was a white crystalline solid (Found: Os, 35·9; Br, 45·0; N, 16·0; μ, 1·8 B.M. Calc. for $[Os(NH_3)_6]Br_3$: Os, 35·7; Br, 45·1; N, 15·8%). The X-ray diffraction data given in Table 1 correspond to the recrystallized product but are essentially identical with those for the crude orange-coloured crystals. (This suggests the presence of only trace impurities in the crude product, which was confirmed by analysis.)

The red filtrate from the initial separation of $[Os(NH_3)_6]Br_3$ (see above) was treated with ca. 0·1 g of solid ammonium bromide and cooled at 0°. The resulting black crystals were filtered, washed with ethanol, and dried *in vacuo* (Found: Os, 27·6; Br, 67·6. Calc. for $(NH_4)_2OsBr_6$: Os, 26·95; Br, 67·9).

Based on the osmium content of the original amber solid, the yields of $[Os(NH_3)_6](OsBr_6)$, and the $[Os(NH_3)_6]Br_3$ and $(NH_4)_2OsBr_6$ derived therefrom were 56, 22, and 16 per cent, respectively, or a total of 94 per cent.

In another case involving a less pure amber ammonia-insoluble product, treatment with 48 per cent HBr at 90° resulted in the anticipated purification of the major component but produced a red filtrate and washings from which a small quantity of fawn-coloured crystals separated upon further addition of ethanol. This product was filtered off, washed with ethanol, and dried *in vacuo* (Found: Os, 37·1; Br, 45·7; N, 13·7; μ, 1·8 B.M. Calc. for $[Os(NH_3)_5Br]Br_2$: Os, 36·9; Br, 46·5; N, 13·6%). X-ray diffraction data for this compound are given elsewhere.[3] The yields of $[Os(NH_3)_6](OsBr_6)$ and $[Os(NH_3)_5Br]Br_2$ in this experiment were 85 and 6 per cent, respectively.

Reactions of hexammineosmium(III) hexabromoösmate(III) with silver ion

In the course of efforts to secure evidence in support of the conclusion that the oxidation state of osmium in the ammonia-insoluble product is 3^+, the interaction of this product with silver ion was investigated. Preliminary experiments showed that treatment of the amber solid with aqueous silver nitrate at room temperature over a period of hours resulted in the successive formation of brown and black solids; after

several hours the characteristic odour of osmium tetroxide was detected. These reactions occur more rapidly at elevated temperatures.

In view of the observations by DWYER and co-workers[6,7] that certain Os^{3+} compounds reduce silver ion to elemental silver, extensive studies were undertaken to determine whether the black product noted above was elemental silver and whether quantitative deposition of silver could be used for an unequivocal establishment of the oxidation state of osmium in the ammonia-insoluble product. In order to exclude the possible oxidizing action of the nitrate ion, saturated silver sulphate solution (0·0542 *N*) was used in these experiments.

In a typical case, 0·1602 g of the amber solid was suspended in ca. 5 ml of water and treated with 10·0 ml of saturated silver sulphate solution [i.e. 3·2 moles of Ag^+/mole of $[Os(NH_3)_6](OsBr_6)$] and stirred for 35 min at 25°. The grey-brown solid was separated from the colourless supernatant solution by filtration and was washed with four 10 ml portions of water. (The combined aqueous filtrate and washings was treated as described below.) Finally, the solid product was washed with ethanol and acetone (Found: Os, 19·2; Ag, 33·8; Br, 43·7%). The magnetic susceptibility per gramme of substance ($\chi_g \times 10^6$) was found to be 1·0; based on the formula Ag_3OsBr_6, $\mu = 1{\cdot}5$ B.M. The yield was 0·1778 g or 53 per cent and 99 per cent based on Os and Br used, respectively. In twelve experiments of this type for which quantitative data (including X-ray diffraction data) were obtained, the $Ag^+/[Os(NH_3)_6](OsBr_6)$ ratio was varied from 3·0 to 10·4, the reaction temperature from 19 to 70°, and the time of contact from 5 to 660 min. The results of these studies are far too detailed for inclusion here. Accordingly, only the following summary is given; the details are available elsewhere.[8] (1) For reactions involving low temperature and short times, reaction was incomplete and X-ray diffraction data showed the presence of unreacted $[Os(NH_3)_6](OsBr_6)$. (2) Reactions at intermediate combinations of time and temperature produced grey-brown solids having compositions that approximated silver(I) hexabromoösmate(III), Ag_3OsBr_6 (Calc: Os, 19·1; Ag, 32·6; Br, 48·3%); in these cases, however, X-ray diffraction data showed the presence of silver bromide. (Efforts to separate the silver bromide by treatment with aqueous ammonia were ineffective owing to the solubility of the osmium compound.) These grey-brown products were characterized by elemental compositions corresponding to the following ratios: Os/Ag = 1 : 2·6–1 : 4·4 (average, 1 : 3·3); Os/Br = 1 : 4·9–1 : 5·6 (average, 1 : 5·4); Ag/Br = 1 : 1·2–1 : 1·9 (average, 1 : 1·6). (3) Reactions at the more elevated temperatures or over longer times (or both) produced black to blue-black mixtures; some of these were diamagnetic and X-ray data showed the presence of elemental silver. In these cases, the formation of OsO_4 was evident. (4) In all of these reactions, the insoluble products accounted for 97–100 per cent of the bromine used as $[Os(NH_3)_6](OsBr_6)$. (5) The grey-brown products accounted for ca. 50 per cent of the osmium used as $[Os(NH_3)_6](OsBr_6)$. (6) In general, the magnetic susceptibility data were inconclusive.

The colourless or pale yellow filtrates and washings from the reactions with silver sulphate solution were treated in several different ways, all of which led to the isolation of hexammineosmium(III) bromide. In a typical case, ca. 50 ml of solution was

[6] F. P. DWYER, R. S. NYHOLM, and B. T. TYSON *J. roy. Soc.* N.S.W. **81**, 272 (1947).
[7] F. P. DWYER and J. W. HOGARTH *Ibid.* **84**, 117 (1951); **85**, 113 (1952); *J. Amer. chem. Soc.* **77**, 6152 (1955).
[8] L. VASKA Dissertation, The University of Texas, Austin, Texas (1956).

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treated with ca. 5 ml of 48 per cent HBr to precipitate any remaining Ag^+ as AgBr which was removed by filtration. The filtrate was evaporated at 80°, whereupon orange-coloured crystals of impure $[Os(NH_3)_6]Br_3$ began to separate. The volume was reduced to 10 ml, 30 ml of ethanol was added, and the solution was cooled to 0°. The resulting solid was recrystallized in the manner described above by dissolution in water followed by addition of ethanol saturated with ammonium bromide. The white crystalline $[Os(NH_3)_6]Br_3$ was identified by analysis, X-ray diffraction pattern, and magnetic susceptibility, all of which were in excellent agreement with the data given elsewhere in this paper. The yields ranged from 38 to 46 per cent, which together with the osmium accounted for in the insoluble product of the initial reaction with silver sulphate leads to a maximum osmium material balance of 98 per cent.

Finally, $[Os(NH_3)_6]Br_3$ was converted to $[Os(NH_3)_6]I_3$ by disolving the bromide in a minimum quantity of water and adding a few drops of 57 per cent hydriodic acid. The yellow solid was filtered, washed with ethanol, and dried over $Mg(ClO_4)_2$ (Found: N, 12·6; μ, 1·7 B.M. Calc. for $[Os(NH_3)_6]I_3$: N, 12·5). X-ray diffraction data are given in Table 1.

DISCUSSION

The evidence given above shows that one-half of the osmium in potassium or ammonium hexabromoösmate(IV) that reacts with liquid ammonia at or near room temperature appears as an ammonia-insoluble solid; the remaining one-half is accounted for by the ammonia-soluble fraction.* Both magnetic susceptibility data and the reactions described above serve to establish beyond reasonable doubt that the oxidation state of osmium in the ammonia-insoluble product is 3^+. Accordingly, Os^{4+} is reduced to Os^{3+} in the reaction with the solvent, and, in the absence of evidence for disproportionation, it is reasonable to assume that nitrogen in solvent molecules is oxidized to $N^{>3-}$. The methods employed in this work were not such as to permit detection of any such oxidation products. Accordingly, we are concerned here primarily with the identity of the Os^{3+} species. On the basis of the data presented, it is reasonable to assume that the Os^{3+} is present in an octahedral d^2sp^3 complex involving one unpaired electron spin.

Evidence in support of the conclusion that the ammonia-insoluble product is hexammineosmium(III) hexabromoösmate(III) was obtained from its behaviour toward hydrobromic acid. The principal reaction that occurs is,

$$[Os(NH_3)_6](OsBr_6) + 3HBr \rightarrow [Os(NH_3)_6]Br_3 + H_3OsBr_6 \qquad (1)$$

For a given quantity of $[Os(NH_3)_6](OsBr_6)$ that reacted in this manner, the yields of each of the proposed products (or derivatives thereof) approached, but in no case accounted for, more that 50 per cent of the osmium. Hexammineosmium(III) bromide was completely characterized; the acid H_3OsBr_6, however, apparently was oxidized upon exposure to the atmosphere;

$$4H_3OsBr_6 + O_2 \rightarrow 4H_2OsBr_6 + 2H_2O \qquad (2)$$

This behaviour, together with the immediate formation of an intensely red solution, is consistent with the known properties of hexahaloösmate(III) complexes.[9,10] This interpretation is supported by the fact that, following separation of $[Os(NH_3)_6]Br_3$,

* The nature of these products will be described in a later paper.

[9] W. R. Crowell, R. K. Brinton and R. F. Evenson *J. Amer. chem. Soc.* **60**, 1105 (1938).

[10] F. P. Dwyer, H. A. McKenzie and R. S. Nyholm *J. roy. Soc.* N.S.W. **80**, 183 (1947).

TABLE 1.—X-RAY DIFFRACTION DATA

K_2OsBr_6		$[Os(NH_3)_6](OsBr_6)$	
d (Å)	I/I_0	d (Å)	I/I_0
6·0	1·00	6·8	0·20
5·2	0·65	5·91	1·00
3·12	0·40	4·18	0·60
2·98	0·75	3·56	0·10
2·58	0·80	3·39	0·30
2·31	0·30	2·86	0·20
1·99	0·20	2·64	0·20
1·83	0·50	2·40	0·30
1·75	0·20	2·08	0·20
1·72	0·20	1·96	0·20
1·49	0·20	1·86	0·10

$[Os(NH_3)_6]Br_3$		$[Os(NH_3)_6]I_3$	
d (Å)	I/I_0	d (Å)	I/I_0
6·2	0·80	6·7	0·20
5·38	0·20	5·7	0·10
4·15	0·10	3·97	1·00
3·80	1·00	2·80	0·20
3·25	0·20	2·30	0·30
2·63	0·20	1·99	0·10
2·19	0·20	1·90	0·10

addition of ammonium bromide led to the isolation of $(NH_4)_2OsBr_6$, i.e.

$$H_2OsBr_6 + 2NH_4Br \rightarrow (NH_4)_2OsBr_6 + 2HBr \quad (3)$$

Although the isolation of bromopentammineosmium(III) bromide might appear to suggest that the amber ammonia-insoluble product contains the isomer $[Os(NH_3)_5Br]$-$[Os(NH_3)Br_5]$, this possibility is ruled out by the data on reactions with silver ion. Accordingly, the formation of $[Os(NH_3)_5Br]Br_2$ must be accounted for by the secondary reaction,

$$[Os(NH_3)_6]Br_3 + HBr \rightarrow [Os(NH_3)_5Br]Br_2 + NH_4Br \quad (4)$$

and it is significant that this product was obtained only following treatment with HBr at elevated temperatures and from dilute solutions from which separation of the bromopentammine compound is favourable relative to the hexammine bromide. Even so, reaction (4) is slow even at elevated temperatures, and quantitative conversion

to the bromopentammine compound was not observed in any case. This is attributable to the great stability of the hexammineosmium(III) ion in strong acid solution, which is to be expected by analogy with the corresponding ruthenium ion.[11] Fragmentary and by no means conclusive evidence[8] suggests that the intensely coloured impurity present in some samples of $[Os(NH_3)_6]Br_3$ prior to recrystallization may be $[Os(NH_3)_4Br_2]Br$.

With reference to the reactions that occur between $[Os(NH_3)_6](OsBr_6)$ and Ag^+, it is noteworthy that in all cases in which the principal reaction (3) appeared to be complete (and irrespective of the experimental conditions employed), the insoluble reaction product accounts for one-half of the osmium and substantially all of the bromine, while the soluble fraction accounts for the remainder of the osmium. These facts establish unequivocally that the total bromine is associated with 50 per cent of the osmium in the co-ordination polymer, which together with the cation–anion ratio of 1 : 1 eliminates numerous possible structures that have the same empirical formula, i.e. Os : Br : N = 1 : 3 : 3. Although silver(I) hexabromoösmate(IV) was not isolated in high purity, there seems little doubt that the principal reaction is

$$[Os(NH_3)_6](OsBr_6) + 3Ag^+ \rightarrow Ag_3(OsBr_6) + [Os(NH_3)_6]^{3+} \quad (5)$$

Contamination of the silver salt with AgBr may result from reactions of Ag^+ with Ag_3OsBr_6 or $[Os(NH_3)_6](OsBr_6)$, in which AgBr is precipitated and anionic species of the type $[Os(OH)_x(Br_{6-x})]^{3-}$ are formed. The appearance of Ag^0 and OsO_4 as products of secondary reactions probably results from decomposition of Ag_3OsBr_6, possibly photochemically,

$$Ag_3(OsBr_6) \rightarrow Ag_2(OsBr_6) + Ag^0 \quad (6)$$

followed by further oxidation of Ag_2OsBr_6 to form OsO_4.* The general decrease in the magnetic susceptibility of these mixtures tends to confirm the observation that an oxidation of osmium(III) occurs as the overall reaction proceeds.

Finally, the isolation of $[Os(NH_3)_6]Br_3$ in yields that account for essentially one-half of the osmium in $[Os(NH_3)_6](OsBr_6)$ that reacts with Ag^+ provides further evidence for the correctness of the conclusion that the initial amber ammonia-insoluble product is indeed hexammineosmium(III) hexabromoösmate(III). The reactions that we observed with Ag^+ are analogous to those that are reported to occur between silver ion and $[Co(NH_3)_6][M^{III}(CN)_6]$, where M^{III} = Fe, Cr, Co, or Mn.[12]

In relation to earlier work[3] it should be noted particularly that both reactions (1) and (5) provide direct routes to the synthesis of salts of the type $[Os(NH_3)_6]X_3$.

* In independent experiments, partial decomposition of silver(I) hexabromoösmate(IV) prepared from $(NH_4)_2OsBr_6$ and Ag_2SO_4 was detected through the appearance of OsO_4 and Ag^0.

[11] H. TAUBE *Chem. Rev.* **50**, 69 (1952).

[12] A. MALAGUTI and T. LABIANKA *Gazz. chim. ital*, **84**, 979 (1954).

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 316 to 331. Pergamon Press Ltd., London

THE CHEMISTRY OF SOME 8-HYDROXYQUINOLINE COMPLEXES OF VANADIUM

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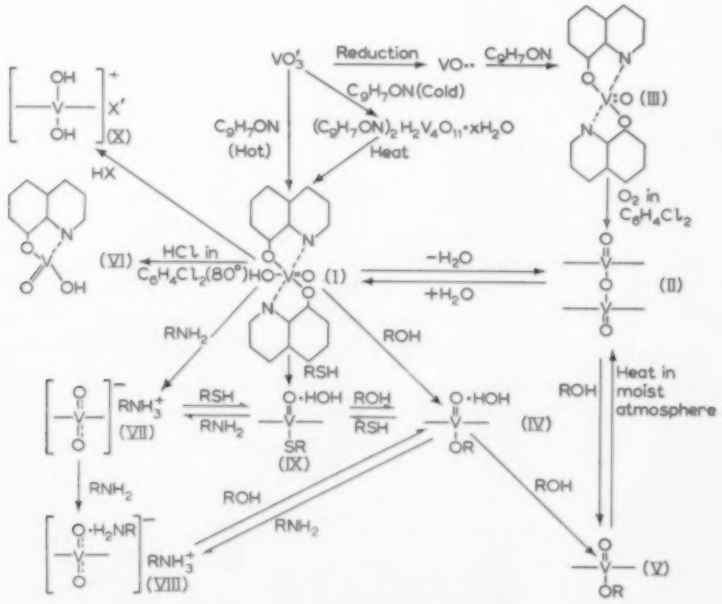
Abstract—Further evidence for assigning "vanadium 8-hydroxyquinolate" the structure oxodi-(8-quinolyloxo)vanadic(V) acid is presented. The reactions of this compound with alcohols, thiols and amines in the pure state and in inert organic solvents, and its reaction with hydrogen chloride in dilute *o*-dichlorobenzene solution are examined and their mechanisms are discussed. A convenient and efficient method of preparation of the "anhydride" of the acid by thermal hydrolysis of its lower alkyl esters is described.

THAT the reaction of vanadate ions with a slight excess of 8-hydroxyquinoline in aqueous solution at pH 5–6 produces relatively complex compounds has been established for some time,[1, 2] but only recently have the structures of the products been assigned with any degree of certainty.[3] The primary product, which can be isolated in the cold, appears to be a yellow condensed vanadate salt of 8-hydroxyquinoline, $(C_9H_7ON)_2 \cdot H_2V_4O_{11} \cdot 2\text{–}5H_2O$. This, on heating, gives, together with vanadium pentoxide, the black "vanadium 8-hydroxyquinolate" which is also obtained by treating vanadate with 8-hydroxyquinoline at pH 5–6 in hot aqueous solution or in hot *o*-dichlorobenzene solution.



General scheme of reactions discussed

[1] N. A. TALVITIE *Analyt. Chem.* **25**, 604 (1953).
[2] R. MONTEQUI and M. GALLEGO *An. Soc. esp. Fis. Quim.* **32**, 134 (1934).
[3] H-J. BIELIG and E. BAYER *Liebigs Ann.* **584**, 96 (1953).

It has been claimed that the black acid **I** is converted quantitatively to the "anhydride" **II** on heating at 250°C.[4] The reaction of **I**, especially in organic solvents, with alcohols to give a red solution has been known for some time.[5] This reaction has been developed as a specific test for alcohols and the analogous reaction with thiols and amines with formation of yellow solutions has been recorded.[6] BIELIG and BAYER[3] propose an explanation, based on somewhat weak experimental evidence, for the formation of the red colour. They conclude that the colour change caused by the action of alcohols on oxodi-(quinolyloxo)vanadic(V) acid can be ascribed to *cis–trans* isomerization. Much of the evidence for this rests on the fact that the elemental analyses of the black acid crystals before and after treatment with alcohols are identical. However, their method of preparation of the solid red compounds by this procedure is such as to lead to the formation of a thin coating of the red compound upon the crystals of the acid **I**: therefore, analysis of the product does not show the presence of the "alcohol" part of the molecule, the presence of which is demonstrated below. In addition, their method of isolation of the red solid after a chromatographic separation is certain to lead to extensive decomposition to **I** with loss of alcohol.

Visual inspection of the acid **I**, the esters **V** and the oxide **II** is inadequate as a means of identification owing to the extreme intensity of the colours which, in the solid state, are almost black and adopt various sheens depending on the method of preparation.

RESULTS AND DISCUSSION

1. *Constitution of the Black Acid I*

The acid was prepared in two ways: (a) 8-hydroxyquinoline in dilute acetic acid was added to a strongly acid solution of pentavalent vanadium at 70–80°C and the mixture was adjusted to pH 5 with aqueous ammonia; (b) 8-hydroxyquinoline in dilute acetic acid was added to a weakly alkaline solution of vanadate at 70°C. Both precipitates were digested adequately and dried at 130°C. Excess organic reagent was removed by extracting with hot benzene. Both products appeared to be identical and underwent identical reactions. Vanadium contents were: (a) 13·66 per cent and (b) 14·07 per cent. (Calculated: for $(C_9H_6ON)_2VO{\cdot}OH$, 13·69 per cent.) The higher vanadium content of (b) was ascribed to co-precipitated vanadium pentoxide, and this may well account for the fact that for some time the black "vanadium 8-hydroxyquinolate" had been assigned the formula bis[oxodi-(8-quinolyloxo)-vanadium(V)] oxide (**II**)[2]. (Calculated for $(C_9H_6ON)_4V_2O_3$, 14·03 per cent.) Although the products are apparently identical in all other respects all subsequent work was carried out on material prepared by method (a).

BIELIG and BAYER[3] confirmed the presence of the hydroxyl group and, probably, the vanadyl group by means of infra-red evidence, and this with the analytical data lead to the formula $[(C_9H_6ON)_2VO{\cdot}OH)]_n$. By carrying out freezing point depression measurements in *o*-dichlorobenzene it has been possible to establish the molecular size: the figure of 380 ± 50 (calculated for **I**, 372; for **II**, 727) assigns n as 1 and clearly differentiates between the possible acid and "anhydride" structures. The results are summarized in Table 1.

[4] M. BORREL and R. PARIS *Analyt. Chim. acta* **4**, 267 (1950).
[5] J. M. BACH and R. A. TRELLES *An. Asoc. quim. argent.* **28**, 111 (1940).
[6] A. J. BLAIR and D. A. PANTONY *Analyt. Chim. acta* **13**, 1 (1955).

TABLE 1.—CRYOSCOPIC DATA FOR OXODI-(8-QUINOLYLOXO)VANADIC(V) ACID IN *o*-DICHLOROBENZENE SOLUTION

Weight of solvent (g)	Weight of naphthalene (g)	Weight of acid (I) (g)	ΔT (C°)	K (°C for 100 g of $C_6H_4Cl_2$)
36·42	0·2054	—	0·310	70·4
36·42	0·2498	—	0·375	70·1
37·7	—	0·0539	0·025	—
40·2	—	0·0241	0·012	—

Examination of the infra-red absorption spectra, recorded with 1 per cent mixtures in pressed potassium bromide discs, showed that the broad band of 8-hydroxyquinoline between approximately 3220 and 2600 cm^{-1} was replaced by a sharp band at approximately 3440 cm^{-1} in the spectrum of the black compound. This presumably represented a change from a chelated hydroxyl bond[7] to a weaker intramolecular hydrogen bonded hydroxyl group. Since no data appeared to be available regarding hydroxyl bond correlations in potassium bromide discs, test experiments were carried out which showed that the hydroxyl bonds of pentaerythrytol and of cetyl alcohol still have frequencies characteristic of polymeric association at 3270–3300 cm^{-1}. The general configuration of the vanadium 8-hydroxyquinoline system is also supported by the presence of new bands at 1106 and 1320 cm^{-1}, which are typical of chelated 8-hydroxyquinoline complexes of other metals.[8]

The structure of the black "vanadium 8-hydroxyquinolate" is therefore that given as **I**, with the hydroxyl group probably hydrogen-bonded to one of the aromatic nitrogen atoms.

2. *Reactions of Oxodi-(8-quinolyloxo)vanadic(V) acid with Alcohols, Thiols and Amines and Properties of the Products*

(a) *Alcohols*

(i) *In the pure reagents.* The black acid dissolves completely in a *large* excess of the boiling lower aliphatic alcohols to give intensely deep red solutions from which red crystals invariably deposit on cooling. These crystals are fairly soluble in most organic solvents, including aromatic hydrocarbons, in marked contrast to the free acid. However, in the course of a short time these solutions slowly deposit the free acid, particularly from concentrated solutions. The solubility and rate of decomposition increase with increasing molecular weight of alcohol.

The analytical data presented in Table 2 immediately suggest that water has been eliminated between the alcohol and the acid with the formation of a compound analogous to an ester, or, in the case of the glycol, a half-ester. Evidence for the formation of an intermediate hydrated ester is discussed in section 2(a)(ii).

The proposed structure of the red crystals is supported by the infra-red spectra of the methanol and ethanol derivatives in which no hydroxyl bonds are observed. Comparisons with discs of the appropriate concentrations of cetyl alcohol in potassium bromide were made to determine the intensity of the hydroxyl group that would

[7] L. J. BELLAMY *Infra-Red Absorption Spectra of Complex Organic Molecules* p. 84. Butterworths, London (1954).
[8] L. J. BELLAMY Private communication.

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have been found if the alcohols had been merely attached by hydrogen bonding to the main 8-hydroxyquinoline complex. This type of linkage would also not be in agreement with the slight shifts from the normal alcohol bands below 1200 cm^{-1} detected in these spectra (e.g. with the methanol derivative, from 1030 to 1040 cm^{-1}; with the ethanol derivative, from 1092–1077 cm^{-1}; from 1050–1025, and from

TABLE 2.—ANALYTICAL DATA FOR SEVERAL OF THE RED ESTERS

Alcohol	Percentage composition					Empirical formulae	
	C	H	N	V	V*	Found	Theoretical*
Methyl	58·93	4·24	7·25	13·12	13·19	$C_{19}H_{16}N_2O_4V$	$C_{19}H_{15}N_2O_4V$
Ethyl	59·46	4·37	7·13	12·71	12·73	$C_{20}H_{17}N_2O_4V$	$C_{20}H_{17}N_2O_4V$
*iso*Propyl	—	—	—	12·30	12·30	—	—
n-Amyl	62·33	5·28	6·48	11·53	11·52	$C_{22}H_{23}N_2O_4V$	$C_{22}H_{23}N_2O_4V$
Allyl	—	—	—	12·33	12·36	—	—
Ethylene glycol	55·18	4·26	6·49	12·07	12·24	$C_{20}H_{17}N_2O_5V$	$C_{20}H_{17}N_2O_5V$

* Calculated figures, based on the ester formulae

880–892 cm^{-1}). Some support for the ester theory may also be provided by the extra band observed, with the ethanol derivative, at 945 cm^{-1}, in the vicinity of the vanadyl band at 952 cm^{-1}. This may well be due to the $V–O–C_{Aliphatic}$ system; in the spectrum of the methanol derivative, the new band may be masked by the V = O band.

Further evidence is provided in the molecular weight determinations of the methanol compound by its depression of the freezing point of benzene and of the ethanol compound by its elevation of the boiling point of ethanol. If the freezing point determination is carried out rapidly and with low concentrations of solute, decomposition is negligible, although precision is not of the highest order. The result of 393 $\pm$ 10 does confirm the molecular size, but does not differentiate between ester formation and simple addition. Elevation of the boiling point measurements of a very precise nature[11] using the ethanol compound dissolved in pure ethanol lead to a figure of 399 $\pm$ 4 (calculated for the ethyl ester, 400).

Clearly, then, the red products obtained in the reaction between pure boiling alcohols and the black acid are the esters oxoalkoxodi(8-quinolyloxo)vanadium(V), and the reaction is not merely geometrical isomerization as suggested elsewhere.[3] This conclusion receives indirect support from the thermo-analytical results given in Section 5.

(ii) *In dilute chlorohydrocarbon solutions.* Provided that there is a fairly large excess of the alcohol, a red colour similar to that obtained in the pure alcohol is produced in dilute (10^{-4} M) solutions in inert media such as tetrachloroethane or *o*-dichlorobenzene.[6] In fact, the visible spectra of the ester in its parent alcohol, of the ester in *o*-dichlorobenzene and of the solution of the acid **I** with an excess of the

[9] S. GLASSTONE, K. J. LAIDLER and H. EYRING, *The Theory of Rate Processes* p. 199. McGraw-Hill, New York (1940).
[10] A. J. BLAIR and D. A. PANTONY *Analyt. chim. acta* **14**, 45 (1956).
[11] N. H. RAY *Trans. Faraday Soc.* **48**, 809 (1952).

alcohol in the same solvent are almost identical (absorption maximum, 500 mμ). However, data presented below show that the product in dilute solution cannot be identical with the ester, although they are very closely related. The character of the product in dilute solution cannot be established directly.

TABLE 3.—EQUILIBRIUM AND RATE DATA FOR THE REACTION BETWEEN CETYL ALCOHOL AND OXODI-(5 : 7-DI-IODO-QUINOLYLOXO)VANADIC(V) ACID AT 30°C

Experiment	Initial concentrations			Equilibrium constant k_e (30°C) (mol^{-1})	Rate constant, k_r (30°C) (l.-mol^{-1} min^{-1})	
	Acid $\times 10^4$ M	Cetyl alcohol $\times 10^3$ M	Water $\times 10^4$ M		by tangents (mean)	by initial rates
1	4·01	4·00	<1	2000	0·171	0·185
2	2·00	4·00	<1	2600	0·183	0·197
3	1·00	4·00	<1	2700	0·195	0·207
4	2·50	2·50	<1	2000	0·220	0·242
5	2·50	5·00	<1	2200	0·153	0·162
6	2·50	10·00	<1	2300	0·140	0·149
7	4·01	10·00	<1	2000	0·146	0·144
8	2·00	10·00	<1	2200	0·137	0·146
9	1·00	10·00	<1	2200	0·151	0·158
10	2·50	6·25	<1	2000	0·139	0·150
11	2·50	12·50	<1	2000	0·130	0·131
12	2·50	25·00	<1	2100	0·134	0·131
13	3·33	4·20	<1	2600	0·152	0·169
14	3·33	8·40	<1	2800	0·129	0·132
15	1·67	4·20	<1	3400	0·151	0·163
16	3·34	4·19	35	3300	0·146	0·155
17	3·34	8·38	35	3500	0·124	0·130
18	1·67	4·19	35	3800	0·140	0·155
19	3·34	4·19	143	2500	0·158	0·178
20	3·34	8·38	143	2700	0·137	0·147
21	1·67	4·19	143	3200	0·148	0·163

Optical densities were measured in 1 cm cells except in experiments 2, 3, 8, 9, 15, 18 and 21 where 2 cm cells were used.

(α) *Equilibrium studies:* For various reasons of experimental convenience, the reaction between *n*-cetyl alcohol and the vanadium(V) complex of 5 : 7-di-iodo-8-hydroxyquinoline (i.e. tetra-iodo-**I**) in *o*-dichlorobenzene was chosen for the investigation of the equilibrium and of the kinetics. The reaction was followed spectrophotometrically at 750 mμ, at which the acid tetra-iodo-**I** has a high absorption, while the red product has a very small absorption. For this small contribution to the whole optical density a correction was made in these and in the rate measurements, the latter being made while equilibrium was being reached.

Results are summarized in Table 3, in which the equilibrium constants are evaluated on the assumption that the equilibrium is that of an addition $A + B \rightleftharpoons C$ (i.e. tetra-iodo-**I** + ROH $\rightleftharpoons$ Red adduct) and even in the presence of relatively high concentrations of water, the values are in tolerable agreement in all cases. Any other assumption of reaction type leads to a considerable divergence from constancy.

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The fact that water, the other product in ester formation, has no appreciable effect on the reaction is particularly significant, as it might be possible to postulate a two-stage reaction in dilute solution, viz.

$$\text{Black acid} + \text{ROH} \rightleftharpoons \text{Adduct} \rightleftharpoons \text{Red ester} + \text{Water}$$

Therefore, in dilute solution the reaction cannot pass the addition compound stage, otherwise water would seriously affect the equilibrium constants as determined above.

(β) *Kinetics data:* The equilibrium data establish that the reaction is probably of the $A + B \rightleftharpoons C$ type. Rate data for the reaction between cetyl alcohol and the tetra-iodo derivative of **I** are summarized in Table 3. Rate constants were evaluated from (a) initial rates, and (b) from concentration-time curves. In the latter method corrections were made for the reverse reaction.

TABLE 4.—EFFECT OF TEMPERATURE ON RATE CONSTANT OF REACTION BETWEEN 5 : 7 : 5′ : 7′-TETRA-IODO-**I** AND CETYL ALCOHOL IN *o*-DICHLOROBENZENE

Experiment	Initial concentrations		Temperature (°C)	Rate constant, k_r ($l \cdot mol^{-1}\ sec^{-1}$) $\times 10^{-3}$
	Acid $\times 10^{-4}$ *M*	Cetyl alcohol $\times 10^{-3}$ *M*		
22(a)	3·35	8·35	20·0	1·075
(b)	3·35	16·7	20·0	0·935
(c)	1·67	8·35	20·0	0·937
23(a)	3·35	8·35	25·0	1·67
(b)	3·35	16·7	25·0	1·45
(c)	1·67	8·35	25·0	1·50
1–21	See Table 3		30·0	2·40 (mean)
24(a)	3·35	8·35	35·0	3·43
(b)	3·35	16·7	35·0	3·22
(c)	1·67	8·35	35·0	3·37
25(a)	3·35	8·35	40·0	5·03
(b)	3·35	16·7	40·0	4·77
(c)	1·67	8·35	40·0	5·03

The reaction is clearly exactly first order with respect both to the alcohol and to the di-iodo-8-hydroxyquinoline complex of vanadium(V). Hence the reaction is bimolecular, and the results lead to a specific rate of 0·0024 litres-mol^{-1} sec^{-1} at 30°C. From the specific rate-temperature relationship (Table 4) it was deduced that the activation energy is 15 cal/mol, and the entropy of activation[9] −19 E.U. Since the solvent had been intensively purified until constant results were obtained, by removing all traces of amines, thiols and acids which are all known to have some effect on the reaction,[3, 6] and no difficulty was encountered in dissolving the complex, it was considered that the results were reliable.

The reaction between cetyl alcohol and oxodi-(8-quinolyloxo)vanadic(V) acid (**I**) was studied similarly by means of a spectrophotometric technique at 700 mμ. The equilibrium and rate results are summarized in Table 5, and the effect of temperature in Table 6. Evidently, the equilibrium is that of an addition reaction which is exactly first order with respect to the alcohol and approximately so with respect to **I**. On

Table 5.—Equilibrium and rate data for the reaction between cetyl alcohol and oxidi-(8-quinolyloxo)vanadic(V) acid in *o*-dichlorobenzene at 30°C

Experiment	Initial concentrations		Equilibrium constant k_e (30°C) (mol^{-1})	Rate constant, k_r (30°C) ($l.\text{-}mol^{-1}\ min^{-1}$)	
	Acid I $\times 10^4$ *M*	Cetyl alcohol $\times 10^3$ *M*		by tangents (mean)	by initial rates
1	3·90	3·905	695	0·434	0·484
2	1·95	3·905	838	0·692	0·627
3	0·976	3·905	796	1·14	1·12
4	2·44	2·441	713	0·488	0·512
5	2·44	4·882	837	0·481	0·484
6	2·44	9·765	682	0·394	0·426

Optical densities were measured in 2 cm cells except in experiment 1 where 1 cm cells were used.

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Table 6.—Effect of temperature on rate constant of reaction between I and cetyl alcohol

Experiment	Temperature (°C)	Rate constant, k_r ($l.\text{-}mol^{-1}\ sec^{-1}$) $\times 10^{-2}$
7(a)	19·7	3·57
(b)	19·7	3·27
8(a)	25·0	5·37
(b)	25·0	5·03
9(a)	30·0	7·95
(b)	30·0	8·45
10(a)	35·0	12·75
(b)	35·0	15·08
11(a)	40·0	19·33
(b)	40·0	20·00

Concentrations used are identical with those of Experiments 5 and 6 in Table 5 for (a) and (b) respectively.

solutions derived from the same masters, the activation energy was found to be 16 cal/mol and the entropy of activation −15 E.U. It is interesting to note that the activation energies of the two reactions studied are almost identical, and the more negative entropy of activation of the tetra-iodo derivative is to be expected from steric considerations.

However, departures from exact bimolecularity and from the Beer–Lambert Law in the second reaction cast some doubt on the accuracy of the results, despite the clear qualitative agreement with the results of the tetra-iodo-I—cetyl alcohol

investigation and the linearity of the $1/T$—log r, relationship. At best, the results of the second reaction can be taken only as an approximation to the true activation data.

These divergencies from constancy of k_a and k_r were ascribed to a decomposition of the acid **I** during its dissolution in *o*-dichlorobenzene, when a residue which appeared to be completely insoluble in that solvent was discovered. This decomposition product would have some indirect effect on the optical properties of the solution and on the equilibrium, and, especially, the rate results. Its nature is discussed in section 4.

(b) *Amines*

The black acid dissolves readily in aliphatic primary and secondary amines to give yellow solutions. Tertiary amines, which are poor solvents, dissolve only a little

TABLE 7.—THERMAL DECOMPOSITION OF THE DI-BUTYLAMINE COMPOUND OF OXODI-(8-QUINOLYLOXO)VANADIC(V) ACID

Temperature (°C)	Percentage loss		Vanadium content	
	Found at constant wt.	Calculated	Found (%)	Calculated (%)
20	—	—	9·75	9·80[a]
90	15·6	14·1[b]	11·5	11·4[c]
170	9·18	16·4[d]	12·8	13·7

Notes: [a] Calculated for $2BuNH_2{\cdot}(C_9H_6ON)_2VO{\cdot}OH$
[b] For loss of one molecule of butylamine
[c] Calculated for $BuNH_2{\cdot}(C_9H_6ON)_2VO{\cdot}OH$
[d] For loss of second molecule of amine

of the acid and give pale green solutions. From the yellow (absorption maximum for *n*-butylamine solution, 390 mμ) solutions in primary amines large yellow crystals were obtained after evaporation and cooling.

Action of heat on the yellow crystals led to the production of a green solid and evolution of approximately half of the combined primary amine, as is illustrated by the thermo-analysis of the butylamine compound. Table 7 summarizes the results obtained during the thermal decomposition of the yellow compound.

Evidently, two molecules of the primary amine are involved, one participating in salt formation with the production of *n*-butylammonium oxodi-(8-quinolyloxo)-vanadate(V) (**VII**), and a second, labile, molecule attached as an amine of crystallization (**VIII**). This second molecule is presumably attached in the case of secondary amines, but not with tertiary amines because these have no active hydrogen atoms for such bonding. Similarly, aromatic amines are poor solvents and give only green solutions.

The first (salt-forming) amine molecule cannot be removed by simple pyrolysis, as on heating above 90°C the green crystals left after removal of the labile molecule

undergo a more fundamental decomposition and the product appears to be a mixture of compounds.

The nature of the bonding of the labile amine molecule may be inferred from the discussion under section 3.

The colour changes brought about by primary, secondary and tertiary amines on oxodi-(8-quinolyloxo)vanadic(V) acid (**I**) in dilute tetrachloroethane and *o*-dichlorobenzene solutions are identical to those produced by the pure liquid amines. Hence, provided that an excess of amine is present, the reactions appear to be identical. In addition, the reaction of **I** with alcohols is strikingly catalysed by aliphatic bases when both alcohol and base are present together, but ultimately the amine reaction becomes predominant.

(c) *Thiols*

On heating the black acid **I** under reflux with an excess of *n*-propyl mercaptan diluted with an equal volume of benzene, a deep yellow-brown solution resulted, from which was isolated a yellow-brown solid. Qualitative analysis showed the presence of sulphur and of vanadium(V) and some vanadium(IV); the material lost mercaptan so readily at room temperature that quantitative elementary analysis gave results of no significance. However, a thermal analysis on the product immediately after isolation and drying showed that a steady loss of mercaptan occurred, increasing with increasing temperature, until constant weight was obtained at 170°C, by which point 12·7 per cent by weight had been lost; evidently, at least 80 per cent of the theoretical quantity of mercaptan for a thiol-ester had been incorporated into the molecule.

The yellow brown solid was completely soluble in benzene but slowly decomposed either by hydrolysis to **I** or by reduction to di-(8-quinolyloxo)vanadium(IV) (**III**) which oxidized in the presence of air to the oxide **II**. This hydrolysed to the final product **I** (see section 5(b)).

After evaporation of the mother liquor from the original preparation, an aliphatic oil, b.p. ca. 190°C, containing a high proportion of sulphur, was isolated. This might well have been di-*n*-propyl disulphide (b.p. 194°C), the expected product of oxidation of the mercaptan by vanadium(V).

In dilute solutions in chlorohydrocarbons, an analogous colour change occurs, but it has already been reported[6] that the products of reaction of **I** with alcohols, thiols and amines are completely interconvertible, provided that a reasonable excess of the reagent is added to the solution already made red with alcohols or yellow with thiols or amines. Hence it appears that in relatively low concentrations of mercaptan, no reduction to vanadium(IV) occurs.

3. *The Nature of the Addition Compounds*

(a) *Alcohol compounds*

In the preceding sections it has been established that the reaction between alcohols and oxodi-(8-quinolyloxo)vanadic(V) acid leads to an addition compound which in the presence of excess alcohol, which may well be acting as a mild dehydrating agent, gives an ester as final product. The simple geometric isomerisation suggested by BIELIG and BAYER[3] is insufficient to explain the facts described in Sections 1 and 2.

Moreover, the black acid **I** (absorption maxima, 340 and 560 mμ) and the red

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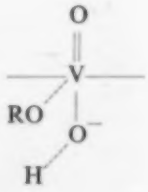
product (absorption maximum, 500 mμ, varying slightly with different alcohols) in dilute solutions are very widely different in spectral and chromatographic properties. It is unlikely that isomerism would cause such a marked difference in light absorption nor explain the fact that **I** is strongly retained, with little decomposition, on activated alumina from organic solvents, while the red compounds are weakly retained and are fairly rapidly decomposed with formation of aluminium 8-hydroxyquinolate. Any hypothesis as to the structure of the red adduct must account for these facts and also consider the remarkable similarity between the spectra of the ester and its intermediate, and the fact that the nature of the reacting alcohol affects, in a small degree, the details of the absorption spectra of both the ester and adduct.

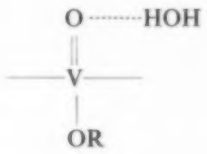
Clearly the formation of the intermediate addition compound and of the ester are closely linked with the hydroxyl group on the central vanadium atom of **I**. The 8-hydroxyquinoline complexes of tetravalent vanadium and titanium, $(C_9H_6ON)_2Ti{=}O$, hexavalent molybdenum $(C_9H_6ON)_2Mo\langle^{O}_{O}$ and uranium $(C_9H_6ON)_2U\langle^{O}_{O}$ and of pentavalent niobium (of probable formula $(C_9H_6ON)_3Nb{=}O$) undergo no obvious reactions with alcohols, thiols or amines. Also, there is marked base catalysis of the reaction of **I** with alcohols in dilute solution and a retardation by acids. Therefore any reaction must involve the participation of the system $-\!\!-\overset{\overset{O}{\cdot\cdot}}{V}\!\!-\!\!-\overset{\cdot}{O}^{-}$. Owing to the geometry of the ion's structure it is probable that the O : V· O′ part of the system is hybridized independently of the main 8-hydroxyquinoline-vanadium system, resulting in $\overset{-}{\overbrace{O\cdots\cdots V\cdots\cdots O}}$. When no base is present the alcohol reaction is slow and probably depends on spontaneous ionization of the proton, this perhaps being assisted by the weakly basic nitrogen atoms in the quinoline residues, and a large excess of alcohol is necessary for any measurable reaction to occur.

To the ion $-\!\!-\!\!\left\{\begin{matrix}O\\ \vdots\\ V\\ \vdots\\ O\end{matrix}\right\}^{-}\!\!-\!\!-$ adds the reagent: it is characteristic of this that it must carry an active hydrogen atom, and reagents without do not react. This was confirmed by passing into an *o*-dichlorobenzene solution of the acid **I** a small quantity of dry hydrogen fluoride. An immediate purple colour, discharged by excess acid, was produced.

The initial reaction thus appears to be an addition across the V·····O′, which might be regarded as analogous to a fully polarized carbonyl group. The initial adduct is, therefore,



This probably undergoes some internal rearrangement with the assembling of a molecule of water which remains attached to the complex by hydrogen bonding, resulting in a hydrated ester,



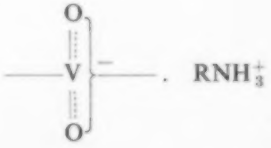
This theory is consistent with the observed kinetics and activation entropy observations and accounts for the relatively ready dehydration to the ester with excess hot alcohol. It seems likely that the visible absorption spectra of the hydrated and anhydrous esters are very similar. Significantly, the theory also explains the failure of **I** to react with water to give an adduct, especially as water might be expected to combine readily because of its strong hydrogen-bonding properties.

Furthermore, it gives an explanation for the relatively greater stability of the tetra-iodo derivative and its lower specific rate of formation when compared with the unsubstituted alcohol compound. It enabled the authors to predict that the 2-methyl homologue would react very sluggishly with the alcohol contained in commercial chloroform to give, if at all, a very unstable adduct. This was confirmed experimentally and applied in the determination of chromium in the presence of vanadium in which the chromium is measured spectrophotometrically as its 8-hydroxyquinaldine complex after chromatographic separation in chloroform–benzene solution.[10]

Thiols probably react in an analogous manner in dilute solutions with the formation of a hydrated thiol ester, but in more concentrated solution a study of the reaction is complicated by the competitive reduction of vanadium(V).

(b) *Amine compounds*

The reaction of **I** is relatively simple. Undoubtedly the first step, common to primary, secondary and tertiary amines, is the formation of a salt, alkylammonium oxodi-(8-quinolyloxo)-vanadate(V) (**VII**), e.g.



To this a second amine molecule, provided that it contains an active hydrogen atom as in primary and secondary amines, adds by hydrogen bonding to the O⋯V⋯O system. Amide formation or addition across the V⋯O bond by the second amine molecule appears to be unlikely because of the relative inactivity of the amine hydrogen atoms. As a consequence, the second amine molecule remains labile, but the first (salt) molecule cannot be removed in a simple manner, by, for example, pyrolysis.

4. *Examination of the Insoluble Product Obtained on Dissolving Oxodi-(8-quinolyloxo(vanadic(V) acid in Hot o-Dichlorobenzene*

The residue mentioned in section 2b(i)α was found only after heating the purified **I** with *o*-dichlorobenzene at 80°C for approximately 48 hr. After filtration and washing with the solvent, there remained an appreciable quantity of yellow green crystals which were insoluble in organic solvents and were only slightly contaminated with its parent acid **I**. Analysis of the yellow green crystals gave the following results on two separately prepared specimens: C, 47·73, 47·77; H, 3·12, 3·04; N, 6·12, ——; V, 21·85, 21·50. This leads to an empirical formula of $C_9H_7O_3NV$. Presence of tetravalent vanadium was proved, and the vanadium was shown to be attached to an 8-hydroxyquinoline residue. The only structural formula that will satisfy these facts is $C_9H_6ON{\cdot}VOOH$, i.e. oxo-8-quinolyloxovanadic(IV) acid (**VI**).

The formation of the vanadium(IV) is readily explained by the presence of chloride ions which were demonstrated to be present in the purified *o*-dichlorobenzene after heating alone at 80°C. The solvent originally contained no impurities except minor quantities of its isomers and a minute trace of water, but during the heating this water caused sufficient hydrolysis for the hydrogen chloride which was produced to reduce the pentavalent vanadium to the tetravalent state with formation of chlorine. This reacted with freed or combined 8-hydroxyquinoline to give phenolic products of an enhanced acidic nature. At the same time half the hydrogen chloride is regenerated to reduce further quantities of vanadium(V) and hence lead to the formation of more **VI**. The slow rate of formation of this very insoluble product results in its homogenous precipitation in a crystalline form, and although the same material is obtained on heating the black acid **I** in *o*-dichlorobenzene with dry hydrogen chloride, the precipitation is so rapid that a finely dispersed product which is difficult to isolate in the pure state is obtained. The development of the blue colour of the inner complex salt X ($X' = Cl'$) indicates that this is an intermediate in the decomposition. The effect of acids such as halogenated phenols on the reaction between alcohols and oxodi(8-quinolyloxo)vanadic(V) acid is known[3] to be retarding. In the solutions investigated for the rate measurements (Section 2(ii)β) the degree of the effect will be different at the different concentrations of **I** arrived at by the various dilutions of the master solutions used in the rate measurements. Hence, the order with respect to the quinolate will not be unity, and will probably be less than one, but the order with respect to cetyl alcohol will not be affected. This was found in practice.

5. *Preparation of bis* [*oxodi-(8-quinolyloxo)vanadium(V)*] *oxide* (*II*)

(a) *Pyrolytically*

It has been stated[4] that the black acid **I** when heated to 250°C, loses the elements of water to yield the oxide **II**. Thermogravimetric analysis of large samples showed this to be unsatisfactory as a method of preparation of **II**; at 175°C, loss of 8-hydroxyquinoline becomes significant and, depending on the rate of heating and compactness of the sample, a range of temperatures of decompositions and percentage weight losses can be obtained. Although the product contains a high proportion of **II** it also contains other decomposition products and analytical data were inconclusive.

A very satisfactory method of preparation was discovered on examining the thermal decomposition of the red esters. These undergo a smooth thermal hydrolysis with loss of the combined alcohol, provided that this has no more than four carbon atoms, leaving a residue of the pure anhydride. As prepared in this way, the oxide is not hygroscopic and is fairly readily soluble in chlorohydrocarbons giving green solutions (absorption maxima, 390 and 540 mμ). In these solutions the bis[oxodi-(8-quinolyloxo)vanadium(V)] oxide is slowly hydrolysed by the traces of water present to give the black acid **I**.

The decomposition data are presented in Table 8. The high losses of the methyl and *iso*propyl esters are accounted for by the volatility of these esters, and the low losses of the amyl ester is due to the involatility of the alcohol and the incomplete decomposition of the ester even at 170°C. The analytical figures confirm the nature of the product, and a crude cryoscopic measurement in *o*-dichlorobenzene indicated the molecular weight to be of the order of 650 $\pm$ 100. Infra-red absorption spectra showed complete absence of bands attributable to hydroxyl groups, and a more intense band at 720 cm^{-1} that might be assigned to the V–O–V system.

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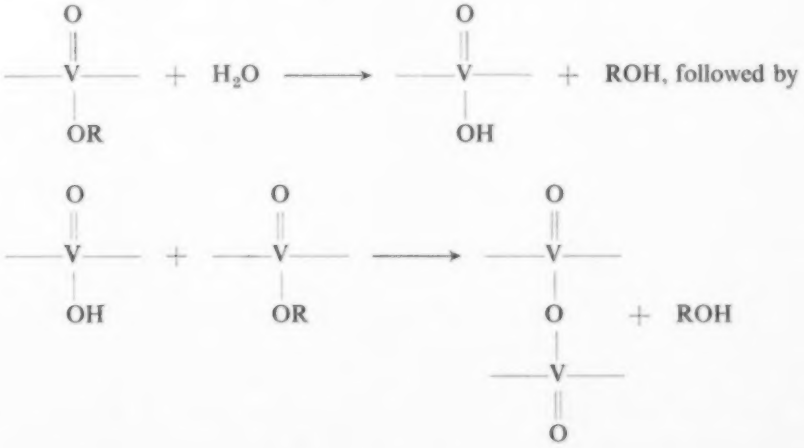
The mechanism of the pyrolytic decomposition must involve the participation of water since the decomposition temperature was raised by at least 10°C when the heating was carried out under a partially dried atmosphere. In order to establish which of the three possible mechanisms of hydrolysis was operative, mixtures of the ester and acid were prepared by grinding together equimolecular quantities: during grinding no alcohol was lost, but, on heating, the theoretical loss for conversion to the oxide **II** was obtained well below the decomposition temperature of the ester alone. This weight loss of the mixture corresponded to that of the second stage of mechanism (i), below:



and from the results summarized in Table 9, it is obvious that the losses agree well with this reaction. If mechanism (ii), involving complete hydrolysis to the acid followed by elimination of water, or (iii), involving hydrolysis and elimination of alcohol from two molecules of ester with simultaneous formation of oxide, were operative, the acid **I** in the experiment on the mixture of acid and ester would be

TABLE 8.—THERMOGRAVIMETRIC ANALYTICAL FIGURES FOR ESTERS OF OXODI-(8-QUINOLYLOXO)VANADIC(V) ACID

Ester	Approximate temperature of start of decomposition (°C)	Weight loss (%)		Vanadium content of residue (%) (Calculated for **II**: 14·03%)
		Found	Calculated*	
Methyl	115	6·91, 6·45, 6·51	5·97	14·06, 14·02, 14·05
Ethyl	95	9·26, 9·61, 9·19	9·21	14·01, 14·03, 13·99
*iso*Propyl	120	12·58	12·58	14·04
n-Amyl	85	16·77	17·91	13·77
Allyl	100	11·77	11·92	13·96

* Figure based on formation of bis[oxodi-(8-quinolyloxo)vanadium(V)] oxide.

TABLE 9.—THERMOGRAVIMETRIC ANALYSIS OF EQUIMOLECULAR MIXTURES OF OXODI-(8-QUINOLYLOXO)VANADIC(V) ACID AND ITS ESTERS

Ester	Approximate temperature of start of decomposition (°C)	Weight loss (%)			
		Found	Calculated for Mechanism		
			(i)	(ii)	(iii)
Methyl	70	4·18, 4·25*	4·22	3·03	3·03
*iso*Propyl	70	7·65, 7·69*	7·64	6·49	6·49

* Heated in dried atmosphere.

completely inert at the low temperature used and, as a consequence, the weight loss would be much smaller. It was concluded that the thermal decomposition of the ester on its own followed a two-stage reaction in which the acid that was first formed by hydrolysis reacted immediately with the residual ester to form the oxide according to the overall mechanism (i), shown above.

Thermal decomposition of the *n*-propyl mercaptan compound and the *n*-butylamine compound gave indefinite final products.

(b) *In solution*

Repeated evaporation of a tetrachloroethane solution of the acid under reduced pressure at 90–100°C also gave the green product identified as the anhydride **II**.

Similarly, when dilute solutions of oxoethoxodi-(8-quinolyloxo)vanadium(V) in very dry *o*-dichlorobenzene were kept under a dry atmosphere, they slowly became green with formation of the oxide **II**, presumably by a mechanism analogous to the thermal decomposition suggested in section (a) above.

The 8-hydroxyquinoline complex of tetravalent vanadium, "vanadyl 8-hydroxyquinolate" (**III**) dissolves in *o*-dichlorobenzene solution to give a yellow colour provided that oxygen is rigidly excluded. However, on the admission of oxygen the

solution becomes green and then, in the presence of moisture, black. In benzene, this solution deposits the black acid **I**. The solution contains pentavalent vanadium and the green and black solutions have all the properties of the "anhydride" and acid respectively. An attempt to prepare the thio analogue of the oxide by adding to the solution a little elemental sulphur dissolved in carbon disulphide met with no success.

EXPERIMENTAL

1. *Preparation of Oxoalkoxodi-(8-quinolyloxo)vanadium(V) esters*

The *methyl*, *ethyl*, iso*propyl* and *allyl esters* were prepared, in 80 to 95 per cent yield by boiling under reflux the oxodi-(8-quinolyloxo)vanadic(V) acid (2 to 5g) with a large excess of the respective alcohol (300 to 800 ml). The hot suspension was filtered and the filtrate allowed to crystallize; in order to economise in the consumption of alcohol and improve the yield, the residue from the first filtration was combined with the mother liquors and the boiling and crystallisation repeated until all the acid **I** had dissolved. The crop of intensely red crystals that were finally obtained was filtered and allowed to stand in air until they were constant in weight and no longer possessed the odour of the alcohol.

The *amyl* and *ethylene glycol* (half-ester) *esters* were prepared by digesting the acid **I** (3 g) with the alcohol (300 ml) at 100°C for 48 hr. After filtration while hot the red solution was allowed to crystallize and the esters were isolated as above in 60 to 65 per cent yield.

Although 0·5 g of the acid **I** appeared to dissolve completely in 800 ml of boiling *tert*-butyl alcohol, and a red powder was obtained after evaporation at room temperature, the product was unstable and readily hydrolysed to the starting materials. Similarly, the acid was found sparingly soluble in cetyl alcohol at 100°C, but soluble with formation of a red solution, in the presence of excess benzene. However, even after evaporation in high (10^{-4} mm) vacuum, no cetyl ester was isolated and only the acid **I** remained.

2. *Cryoscopic Measurements*

(*a*) *Freezing-point depression*

These measurements were carried out with standard techniques, the solvents being dried fairly carefully before use. Measurements in *o*-dichlorobenzene (f.p. −18°C) were made in a solid carbon dioxide–acetone bath that was maintained at an even temperature by cautious addition of the carbon dioxide. Although a calcium chloride guard-tube was employed no other special precautions over exclusion of moisture were deemed necessary as it was considered that at −18°C the water would be completely inert in this system.

(b) *Boiling-point elevation*

The boiling-point determination was carried out in an apparatus essentially similar to that of RAY[11] with minor local improvements designed to increase the precision to ±1 per cent. Purified acetanilide, stilbene and cholestryl acetate were used as reference compounds.

3. *Infra-red Spectra*

Measurements were made by the pressed disc technique in a double beam infra red spectrophotometer,[12] the discs being 200 mg of dried potassium bromide containing 2 mg of substance. A few spectra were also kindly run by Mr. L. THOMAS at C.D.E.E., Porton, on a Perkin–Elmer 21-G instrument.

4. *Thermogravimetric Analyses*

The thermal decompositions, at various heating rates, were followed on a Stanton S1 recording balance, from the rear pan of which was suspended a platinum dish containing the sample heated in an air oven. In order to avoid stray convection heating of the balance the suspension wire passed through a series of very small holes in baffles including a water-cooled plate much larger in area than the balance. Owing to the small losses encountered and the high precisions required in this work,

large sample weights were taken: in order to allow reasonable access of the whole sample to the air, the sample was spread in a large dish. Expedients were employed to counter false weight changes due to convection currents and electrostatic effects, and all weight losses were related to a blank. When dried gases were lead into the heating chamber, the gas flow was baffled with glass wool packing.

5. *Spectrophotometry and Kinetics Measurements*

(a) *Instrument*

All absorption measurements were made in a Unicam SP600 spectrophotometer.

(b) *Purification of reagents*

(i) O-*Dichlorobenzene*. The commercial solvent was purified by successive distillation, repeated washing with dilute (1 + 1) hydrochloric acid and 15 per cent aq. sodium hydroxide, and prolonged boiling with dilute alkaline potassium permanganate. The sequence was repeated and the roughly dried product was distilled. The collected fraction b.p. 181·5–182·5°C, was dried over calcium chloride and then magnesium perchlorate.

(ii) 8-*Hydroxyquinoline complexes*. These were prepared by standard methods from aqueous (pH 5–7) ammonium vanadate and 8-hydroxyquinoline in dilute acetic acid or 5 : 7-di-iodo-8-hydroxyquinoline in dioxane. The dried products were washed with hot benzene and dried to constant weight at 120°C.

(iii) *Cetyl alcohol*. The commercially pure product was crystallised repeatedly from 40–60 petroleum ether until constant in melting point (48°C).

(c) *Method of following the reactions*

The calculated quantities of reagents were mixed and small quantities were removed from time to time for optical density measurements. Due to the low speeds of all reactions investigated it was concluded that no error was entailed from returning the measurement specimens to the bulk in the flask in the thermostat bath. Temperature control in all cases was to within ±0·02°C.

6. *Vanadium Analyses*

Ignition to vanadium pentoxide as the weighing form was abandoned as a method of analysis owing to the appreciable volatilization losses of the complexes even when the ignition was conducted under oxalic acid. A titrimetric method[12] involving quantitative reduction of vanadium(V) to vanadium(IV) with standard ferrous solution after an oxidative destruction of organic matter was employed.

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[12] G. J. MINKOFF *Fuel* **29**, 228 (1950).
[12] *Standard Methods of Iron, Steel and Ferro-Alloys* p. 86. The United Steels Companies, Sheffield (1951).

J. Inorg. Nucl. Chem., 1958, Vol. 5, pp. 332 to 338. Pergamon Press Ltd., London

ION EXCHANGE BEHAVIOUR AND DISSOCIATION CONSTANTS OF AMERICIUM, CURIUM, AND CALIFORNIUM COMPLEXES WITH ETHYLENEDIAMINETETRA-ACETIC ACID

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Abstract—Separation factors between californium, curium, and americium on ion exchange resin Dowex-50 X-12, in ammonium form, have been calculated from static equilibrations between pH 2 and pH 3·3 in presence of EDTA 10^{-2} M.

They are found to be 2·04 ± 0·05 between americium and curium and 5·5 ± 0·1 between curium and californium.

In the experimental conditions, only 1 : 1 complexes are formed, and by ion exchange techniques, the dissociation constants are found to be equal to:

Californium:	$10^{-19\cdot09\pm0\cdot2}$
Curium:	$10^{-18\cdot45\pm0\cdot1}$
Americium:	$10^{-18\cdot16\pm0\cdot1}$

Preliminary column experiments show that this complexing agent will be quite useful for separating actinide elements.

THE dissociation constants of the complexes between actinide elements and ethylenediaminetetra-acetic acid (EDTA) have not yet been determined, except for Th^{+4} complex, studied polarographically by SCHWARZENBACH,[1] and Pu^{+3}, Pu^{+4}, PuO_2^{+2} complexes studied by FOREMAN and SMITH,[2] using the ion exchange technique.

In the present work we have tried to evaluate the usefulness of EDTA as a complexing agent for separating trivalent actinide elements on an ion exchange column and to determine the dissociation constants of Am^{+3}, Cm^{+3}, and Cf^{+3} complexes. As EDTA is a tetra-basic acid, we shall write it in the usual form H_4Y.

As demonstrated by our results only 1 : 1 complexes (MeY^-) are formed in our experimental conditions. Such complexes are well known for lanthanide elements,[3,4] and FOREMAN and SMITH[2] have demonstrated that the complex formed with Pu^{+3} is PuY^- in analogous conditions.

The equilibrium involving this complex formation is:

$$MeY^- \rightleftarrows Me^{+3} + Y^{-4} \quad \frac{[Me^{3+}][Y^{-4}]}{[MeY^-]} = K_c \qquad (1)$$

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(1) G. SCHWARZENBACH, R. GUT and G. ANDEREGG *Helv. chim. acta* **37**, 937 (1954).
(2) J. K. FOREMAN and T. D. SMITH *The Nature and Stability of the Complexes Formed by the Ions of Tri-, Tetra-, and Hexa-valent Plutonium with EDTA*: I.G.O.-R/W 10, Windscale Works, Sellafield, England (1956).
(3) G. SCHWARZENBACH and E. FREITAG *Helv. chim. acta* **34**, 1503 (1951).
(4) E. J. WHEELWRIGHT, F. H. SPEDDING and G. SCHWARZENBACH *J. Amer. chem. Soc.* **75**, 4196 (1953).

where square brackets represent molar concentrations. K_c is called the dissociation constant of the complex. Such a negative complex will not absorb on a cation exchange resin such as Dowex-50, whereas Me^{3+} will do so. We shall call K_d, the distribution coefficient of the actinide ion between the resin and the solution, at equilibrium: we have, by definition

$$K_d = \frac{\text{the total amount of actinide on the resin}}{\text{the total amount of actinide in solution}} \times \frac{\text{ml of solution}}{\text{g of dry resin}} \tag{2}$$

In terms of radioactive measurements, K_d expression becomes:

$$K_d = \frac{\text{counts/min (total)} - \text{counts/min (solution)}}{\text{counts/min (solution)}} \times \frac{\text{ml of solution}}{\text{g of dry resin}} \tag{3}$$

where counts/min (total) is the total activity introduced in solution, and counts/min (solution), the activity remaining in solution after the equilibrium has been reached.

As usual, we call "separation factor α" between two ions A and B, the ratio K_d^A/K_d^B. In the particular case of EDTA ligand it is easy to demonstrate that K_d expression becomes:

$$K_d = K_d^\circ \cdot \frac{1}{1 + \dfrac{[H_4Y]_t}{\theta \cdot K_c}} \tag{4}$$

where K_d° is the distribution coefficient of Me^{+3} ion in the absence of a complexing agent, all other conditions remaining the same; $[H_4Y]_t$ is the total concentration in moles/l. of EDTA introduced in solution; K_c is the dissociation constant of the $[MeY^-]$ actinide complex; and θ is a function of the pH and of the four acid dissociation constants of EDTA:

$$\theta = 1 + \frac{[H^+]}{K_4} + \frac{[H^+]^2}{K_4 \cdot K_3} + \frac{[H^+]^3}{K_4 \cdot K_3 \cdot K_2} + \frac{[H^+]^4}{K_4 \cdot K_3 \cdot K_2 \cdot K_1} \tag{4a}$$

Thus, if we can determine K_d and K_d° in the same range of pH and the same conditions, and provided we know θ from the acid dissociation constants of EDTA, we are able to calculate for each plot of K_d the dissociation constant K_c.

EXPERIMENTAL

Apparatus and reagents

All these experiments were made at 25°C ± 0·02 by stirring a well-known amount of resin with a solution containing a fixed concentration of EDTA and the tracer. Experience shows that equilibrium between resin and solution was obtained in less than half an hour. Nevertheless, equilibration was usually allowed to continue overnight.

Dowex-50 X-12 resin was used in ammonium form. First, this resin was graded to settle, in acid form, at 0·75–1·25 cm/min in water. Six successive gradings were made in order to eliminate coarse, and, above all very small particles which might have given trouble in some of these experiments.

By successive column washings with 6 M HCl, conductivity water, 6 M NH_4OH, $2{\cdot}5 \times 10^{-2}$ M EDTA at pH 4·2, and finally, conductivity water, a batch of resin of spectrographic purity was obtained.

The resin was dried overnight at 105–110°C and kept in a vacuum desiccator. The resin was weighed in closed glass weighing bottles, in order to prevent any absorption of moisture. Samples were equilibrated in ground glass-stoppered 12 ml cones (sealed with Dow Chemical silicone grease), attached to a rotating wheel immersed in the thermostatic bath. The pH-meter used was the Beckman Model G, standardized at pH 4·00 with a commercial Beckman buffer and with a specially prepared potassium acid phthalate buffer. Special care was taken with pH measurements, because pH is the most important factor in determining K_d values. The pH-meter was standardized several times during each series of measurements. Measurements were taken of each individual solution, after equilibrium had been reached, with an accuracy of 0·01 pH unit. The EDTA was obtained in C.P. grade from Bersworth Chemical Company, Framingham, Mass. No impurities were detected in a 1 mg sample by arc and spark spectrographic analysis. All other reagents were of analytical grade. Glassware was boiled with HNO_3 6 N, then washed with conductivity water. Alpha counting was done in the usual 2π alpha chambers with a proportional counter. Except for equilibration at 25°C, all the manipulations (including pH measurements) with activities higher than 10^5–10^6 counts/min were made in a Berkeley box.

Solutions and tracers

Solutions to be equilibrated were made exactly 10^{-3} M in EDTA by adding to the solid a known amount of a standardized NH_4OH solution (to obtain pH 4·50), and were than made exactly 0·1 M in NH_4^+ by adding NH_4ClO_4. The tracer was added in several drops of 0·05 M $HClO_4$ solution. Then, for each sample, the pH was adjusted to the desired value with small quantities of $HClO_4$. The solutions used in K_d° measurements were 0·1 M in NH_4ClO_4. The pH was adjusted in the same way. For these equilibrations, very small quantities of resin were used: 2–10 mg weighed to $\pm$0·005 mg in small closed containers with an Ainsworth Model V.M. Balance. For K_d measurements quantities of resin varied from 30 mg to 500 mg. Usually, for each equilibration exactly 10 ml of solution were used. The tracers involved were Am^{241}, Cm^{244} + 0·2 per cent by mass Cm^{242}, and Cf^{252}. Spectrographic and pulse height analysis showed that these tracers were pure chemically and radiochemically.

Mounting the plates and sample counting

Unless otherwise indicated, activity measurements were made at equilibrium from the solution phase. After a short time of settling, aliquots of the solutions were taken by means of a transfer pipette with a tight glass wool plug in the tip (in order to filter small particles of resin from the aliquot); then the tip was broken off and the aliquot transferred into a small container; occasionally two aliquots were picked up with two different pipettes to check the absence of fluctations which would indicate that some small quantities of resin were passing through the plug. In order to perform this pipetting it was necessary to connect the pipette to a vacuum line.

Samples of 50 λ (or 100 λ for californium) of the aliquots were mounted on platinum plates and dried slowly under a heat lamp. Continued heating resulted in evaporation of NH_4ClO_4. The plates were not flamed, since this sometimes led

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to losses of about 5 per cent. At least two plates were prepared and counted for the same equilibration (occasionally from two different aliquots).

By means of long counting times, the statistical error was kept below 1 per cent except for the lowest counting rates. The fluctuation between two different plates from the same equilibration was usually in the range of the statistical error (calculated as σ); when this was not the case, new plates were mounted.

RESULTS AND DISCUSSION

K_d determinations

At 10^{-3} M EDTA concentration, the suitable range for K_d measurements was found between pH 2 and pH 3·3. Results are shown in Fig. 1. The lowest point on each curium and americium plot are less accurate ($\pm$10 per cent) and were not used for dissociation constant determinations.

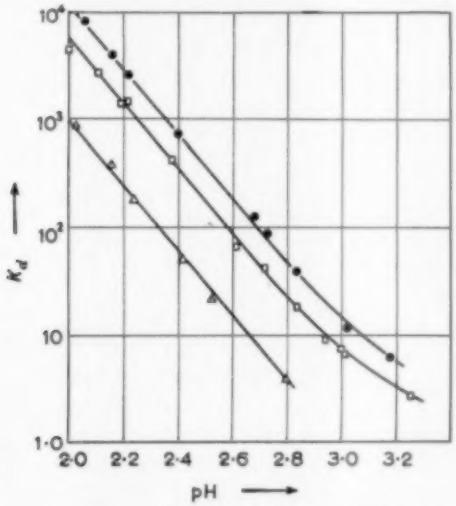

FIG. 1.—K_d vs. pH — 25°C.
Solution: 10^{-3} M EDTA — 0·1 M NH_4ClO_4.
Resin: Dowex-50 X-12, ammonium form.
● Americium
□ Curium
△ Californium

The separation factors calculated from Fig. 1, are:

$$\alpha_1 = \frac{K_d^{Am}}{K_d^{Cm}} = 2{\cdot}04 \pm 0{\cdot}05$$

$$\alpha_2 = \frac{K_d^{Cm}}{K_d^{Cf}} = 5{\cdot}5 \pm 0{\cdot}1$$

These values can be favourably compared with those obtained by column method Dowex-50 X-12 with alpha-hydroxy*iso*butyric acid.[5]

$$\alpha_1 = 1{\cdot}4$$

$$\alpha_2 = 5{\cdot}0$$

[5] G. R. CHOPPIN, B. G. HARVEY and S. G. THOMPSON *J. inorg. nucl. Chem.* **2**, 66 (1956).

K_d° determinations

These results are shown in Fig. 2. Some fluctuations are observed in the plots, the largest deviation being about 5 per cent from the curve. Because of high K_d° values, the quantities of active isotopes used for these equilibrations were rather important: for ^{241}Am, on the order of 2·8 μg Am/10 ml. Nevertheless, it is easy to calculate that this concentration of americium can saturate less than 0·5 per cent of the smallest quantity of resin used (2 mg).

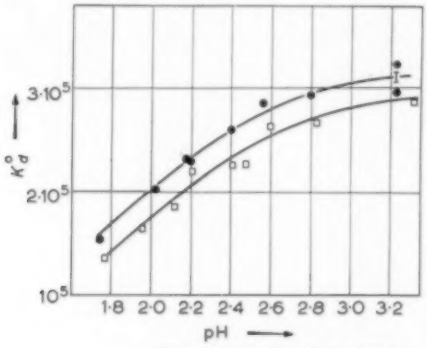

FIG. 2.—K_d° vs. pH — 25°C.
Solution: 0·1 M NH_4ClO_4.
Resin: Dowex-50 X-12, ammonium form.
● Americium
□ Curium

Stability constants

The four apparent acid dissociation constants of EDTA were determined by SCHWARZENBACH and ACKERMANN[6] and by CABELL[7] by potentiometric measurements at 20°C in 0·1 M KCl solutions. CARINI and MARTELL[8] have studied the influence of the ionic strength (KCl) on EDTA dissociation constants. All these results are substantially similar, SCHWARZENBACH's values being somewhat higher.

For our calculations we have chosen CABELL's values, which are $pK_1 = 2{\cdot}24_1$; $pK_2 = 2{\cdot}95_1$; $pK_3 = 6{\cdot}24_0$, and $pK_4 = 10{\cdot}31_6$.

In the range of our measurements, formula (4) can be simplified:

$$\frac{K_d}{K_d^\circ} = \frac{\theta \,.\, K_c}{[H_4Y]_t} \tag{5}$$

Thus, a plot of K_d/K_d° vs. pH must have the same slope as a plot of θ vs. pH. A perfect agreement was observed, and this is the best proof that our assumption of the form 1 : 1 of the complexes is correct.

While the quoted dissociation constants for EDTA were determined at 20°C, our measurements were made at 25°C. Nevertheless, from MARTELL and co-workers' data on the influence of temperature on the third and fourth dissociation constants of EDTA,[9] on the dissociation constants of the analogue nitrilotriacetic acid[10]

[6] G. SCHWARZENBACH and H. ACKERMANN *Helv. chim. acta* **30**, 1798 (1947).
[7] M. J. CABELL *The Complex Ions Formed by Thorium and Uranium with Complexones* AERE C/R 813 Ministry of Supply, Harwell, Berkshire, England (1951); *Analyst.* **77**, 859 (1952).
[8] F. F. CARINI and A. E. MARTELL *J. Amer. chem. Soc.* **74**, 5745 (1952).
[9] F. F. CARINI and A. E. MARTELL *J. Amer. chem. Soc.* **75**, 4810 (1953).
[10] V. L. HUGHES and A. E. MARTELL *J. Amer. chem. Soc.* **78**, 1319 (1956).

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TABLE 1

Element	pH of K_d plot ±0·01 unit	K_d value	$K_d^\circ \times 10^{-5}$ from curve 2	Actinide dissociation constant	
				$\theta \times 10^{-10}$ from CABELL's EDTA values	pK_c
Americium	2·06	8,190	2·11	5,700	18·16
	2·16	4,100	2·25	2,550	18·15
	2·22	2,640	2·35	1,610	18·15
	2·40	750	2·59	426	18·17
	2·68	128	2·88	55·5	18·11
	2·72	89·5	2·91	44	18·14
	2·83	39·8	2·97	20·3	18·18
	3·02	11·6	3·05	6·4	18·23
					Average 18·16
Curium	2·00	4,620	1·75	9,175	18·54
	2·11	2,780	1·93	3,700	18·41
	2·19	1,370	2·05	2,050	18·48
	2·22	1,480	2·09	1,610	18·36
	2·38	430	2·31	477	18·41
	2·62	69·4	2·57	84	18·49
	2·72	45·4	2·64	44·0	18·41
	2·84	18·7	2·73	19·8	18·46
	2·94	9·09	2·76	10·4	18·50
	3·00	7·51	2·81	7·4	18·44
	3·01	7·04	2·82	6·7	18·43
			$K_d^\circ \times 10^{-5}$ calculated		Average 18·45
Californium	2·03	909	1·38	7,300	19·14
	2·16	314	1·48	2,550	18·98
	2·24	192	1·58	1,380	19·06
	2·42	51·0	1·84	360	19·11
	2·53	22·9	1·98	157	19·13
	2·80	4·00	2·21	25·4	19·15
					Average 19·09

and other amino acid analogues,[11] it can be seen that the change in θ function of EDTA between 20°C and 25°C will affect the actinide dissociation constant of less than 0·05 pK_c unit.

The reason we have chosen NH_4ClO_4 to obtain an ionic strength equal to 0·1 is that ClO_4^- ions complex actinide ions little, if at all, whereas Cl^- ions do.[12,13]

Moreover, NH_4ClO_4 can be easily destroyed by heating without leaving a residue, and this facilitates the radioactivity measurements.

[11] N. E. OCKERBLOM and A. E. MARTELL *J. Amer. chem. Soc.* **78**, 267 (1956).
[12] G. T. SEABORG, J. J. KATZ and W. M. MANNING *The Transuranium Elements* N.N.E.S. Div. IV. Vol. 14B, Paper 4.4. McGraw-Hill, New York (1949).
[13] M. WARD and G. A. WELCH *J. inorg. nucl. Chem.* **2**, 395 (1956).

K_d° values in Table 1 are taken from Fig. 2. We had no opportunity to determine K_d° for californium; we calculated these values, assuming that the difference between $K_d^{\circ Cm}$ and $K_d^{\circ Cf}$ is twice the difference $K_d^{\circ Am} - K_d^{\circ Cm}$ in other words:

$$K_d^{\circ Cf} \simeq K_d^{\circ Cm} - 2(K_d^{\circ Am} - K_d^{\circ Cm}) \quad (6)$$

As shown by SURLS,[14] using Dowex-50 X-4 resin, K_d° values for the lanthanide elements, americium and curium, depend essentially on the ionic radii. This interpolation allows us to estimate K_e for the californium to within $\pm 0{\cdot}2 pK_e$ unit. For americium and curium dissociation constants, we estimate an error at $\pm 0{\cdot}1 pK_e$ unit.

FOREMAN and SMITH[2] give for the dissociation constant of Pu^{+3} complex: $pK_e = 18{\cdot}12 \pm 0{\cdot}1$, calculated from CABELL's EDTA dissociation constants in comparison with our pK_e value for Am^{+3} complex, that for Pu^{+3} is somewhat higher than might be expected. Nevertheless, we think that the agreement is satisfying, considering the fact that these authors made their determinations in 0·1 M KCl at 20°C, whereas ours were made in 0·1 M NH_4ClO_4 at 25°C.

Column separation experiments

Few experiments have been done, but all show that californium, curium, and americium behave in the same way as do heavier lanthanide elements, and that the exchange reaction between complex in solution and resin phase is fast enough so that EDTA can be used quite effectively for column separation of actinides. At any rate, theoretical separation factors do not seem to be overestimated. Another important fact that should be pointed out is that, on the basis of stability constants, EDTA should be a useful complexing agent for the separation of the heaviest actinide elements from rare-earth fission products.

Acknowledgements—I wish to express my appreciation to Prof. GLENN T. SEABORG for making possible my stay at the Radiation Laboratory. I should like to thank Prof. BURRIS B. CUNNINGHAM for many helpful discussions and suggestions during the course of this work, Dr. STANLEY G. THOMPSON and Dr. JAMES C. WALLMANN for time spent in useful discussions, and Miss LILY GODA for technical help in some experiments.

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[14] J. P. SURLS *Ion Exchange Behavior of Actinides and Lanthanides* (Thesis). University of California Radiation Laboratory, UCRL-3209 (1956).

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LETTERS TO THE EDITORS

The preparation and properties of sodium gold azide

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RECENT predictions of some properties of aurous azide by EVANS and YOFFE[1] have made it desirable to attempt the preparation of that compound.

An azide of gold has been reported by CURTIUS and RISSOM[2] who obtained long orange needles on evaporating a solution obtained by mixing solutions of gold chloride and sodium azide. They reported that that part of the crystals which redissolved in water was very dangerous and that a drop of the solution exploded with violence when heated. They considered the compound to be AuN_3 but offered no evidence to support this.

While investigating possible methods of preparing aurous azide a new sodium gold azide has been prepared and its properties investigated.

Preparation of sodium gold azide

This compound has been prepared by treating a solution of auric chloride in ether with dry sodium azide. 0·1 g of Johnson Matthey gold chloride ($HAuCl_4$) were dissolved in 10 ml of 9 per cent hydrochloric acid and the gold chloride extracted with several 5 ml portions of diethyl ether. The ethereal solution, in all ca. 25 ml, was transferred to a corked flask containing a substantial excess of dry recrystallized sodium azide. The colour of the solution changed rapidly from the bright yellow of gold chloride to a deeper red brown suggesting that considerable immediate reaction occurred. After standing with intermittent shaking for a few hours the solution was transferred to fresh sodium azide and allowed to stand overnight. (A small amount of gold may be precipitated at this stage.) The solution was filtered and evaporated to dryness at room temperature. Stainless steel or platinum vessels were used for this and subsequent steps in the preparation to minimize explosion hazards.

The compound separated as orange-red needles only slightly soluble in dry ether. The crystals were washed with several small portions of sodium-dried ether to remove any unchanged gold chloride. Finally the crystals were redissolved in 5–10 ml absolute alcohol, the solution filtered if necessary and evaporated to dryness at room temperature. The orange needles are readily decomposed by light and are extremely soluble in water so that evaporation of the solutions must be carried out in the dark and in a dry atmosphere.

Samples of the compound prepared as above have been analysed qualitatively for the presence of some likely impurities. The crystals dissolved completely in ethyl alcohol and water giving clear solutions containing only a very few particles just visible at ×600 magnification. Small crystals were treated with very dilute aqueous sodium nitrite acidified with acetic acid. The orange solution first formed decolorized rapidly with the evolution of gas and the deposition of metallic gold. When the resulting solution was treated with acid silver nitrate a precipitate of silver acetate formed initially and later redissolved, but no trace of silver chloride was found. Blank experiments showed that it was not easy to detect the very fine silver chloride precipitate under these conditions but 5 per cent gold chloride as impurity should have been detected. Using potassium iodide and starch, no chlorine could be detected in the gaseous products of complete decomposition.

The microscopic examination of the crystals and the results of the qualitative analysis provide strong evidence that the orange-red crystals are a pure compound sensibly free from excess sodium azide, gold chloride, and uncombined gold.

Determination of empirical formula.

The compound has been analysed quantitatively for gold, nitrogen, and sodium. Weighed samples were decomposed thermally in a constant volume system. The resultant gold was weighed and the

[1] TH. CURTIUS and J. RISSOM *J. prakt. Chem.* **58**, 304 (1898).
[2] B. L. EVANS and A. D. YOFFE *Proc. roy. Soc.* **238**, 568 (1957).

pressure of nitrogen evolved measured at a constant known temperature on a calibrated McLeod gauge. At 117°C decomposition proceeded smoothly at a rate such that a two mg sample was decomposed completely in about 60 min.

Raising the temperature to ca. 190°C produced no further increase in pressure. Three independent preparations have been analysed. The mean values for the three preparations were.

Gold 63·9 ± 0·5 per cent;
Nitrogen 28·6 ± 0·2 per cent,

where the limits quoted include the full spread of the experimental results.

No change in weight occurred when a fresh sample was kept *in vacuo* for 1½ hr at room temperature or when the product gold was heated to ca. 200°C in air. A very slight (unweighable) sublimate formed on the cooler parts of the tube, during the decomposition.

The sodium was determined using an Evans Electroselenium flame photometer. The sodium content of a known aqueous solution of the compound was compared with standard solutions of sodium chloride. This gave the sodium content of the azide as 5·2 ± 0·2 per cent. No evidence could be found to suggest that the crystals contain any solvent of crystallization.

The mean composition of the crystals may be taken as: Gold 63·9 per cent; nitrogen 28·6 per cent; sodium 5·2 per cent; Total 97·7 per cent.

The very explosive nature of the crystals necessitated using only small quantities (ca. 2·0 mg) for the analyses. Under these circumstances an over-all material balance within 3 per cent can be considered acceptable.

The above composition gives an empirical formula of $NaAu_{1\cdot42}N_{9\cdot05}$

Properties

The compound crystallizes as soft orange-red needles very soluble in water, ethyl alcohol, and acetone. It can be recrystallized from ethyl alcohol and acetone without change. It is slightly soluble in dry ether and insoluble in chloroform and carbon tetrachloride. A preliminary X-ray investigation of the crystals suggests an orthorhombic cell.

The compound can decompose slowly and explosively on heating. Decomposition occurs at a measurable rate at 90°C and is rapid at 117°C. Explosion occurs at temperatures in the region of 130°C.

Aqueous solutions are unstable, and decompose slowly on standing in subdued light for 3–4 days giving a blue-gold colloid. A solution reacts with sodium nitrite and acetic acid giving nitrogen and gold.

Discussion

The microscopic examination of the crystals, the results of the qualitative analysis and the constancy of composition of independent preparations suggest strongly that the orange-red crystals are a pure substance. The at. ratio of gold to sodium, 1·43, is somewhat surprising. Unfortunately the difficulties of the quantitative analysis introduce some uncertainty, particularly in the gold/sodium ratio. Two extreme values for this ratio may be obtained by assuming that the total analytical discrepancy, 2·3 per cent, represents either lost gold or sodium. This gives values of 1·49 and 0·99 respectively. A consideration of the analytical errors strongly favours the higher value giving the empirical formula, $NaAu_{1\cdot5}N_9$. However, since the lower value gives an empirical formula $NaAuN_9$, which is less difficult to interpret, this possibility should also be considered.

The method of preparation, thermal decomposition characteristics and reaction with sodium nitrite and acetic acid indicate clearly that the compound contains the azide radical.

It is not possible at this stage to make any statements concerning the detailed structure of the compound, particularly as thermodynamic calculation suggests that the azide ion is capable of reducing Au (III) to Au (I).

Acknowledgements—I am pleased to be able to thank Dr. A. D. Yoffe for his interest and many helpful discussions and Dr. C. B. Amphlett, Chemistry Division, A.E.R.E., for the loan of a flame photometer.

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Some cation exchange properties of ammonium 12-molybdophosphate

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THE occurrence of base exchange in ammonium 12-molybdophosphate when washed with potassium nitrate solution has been suggested by BAXTER and GRIFFIN[1] and THISTLETHWAITE.[2] NYDAHL has been reported by LINDQVIST[3] as having found this salt to be an efficient ion-exchanger of potassium, rubidium and caesium ions, but no results appear to have been published.

The generally accepted formula of ammonium 12-molybdophosphate (hereafter abbreviated to AMP) is $(NH_4)_3[PMo_{12}O_{40}]$ which is derived from 12-molybdophosphoric acid $H_3[PMo_{12}O_{40}]$. ILLINGWORTH and KEGGIN[4] showed, by X-ray powder photographs, that 12-molybdophosphoric acid and its ammonium, sodium, potassium, rubidium, caesium and thallium salts all have the same fundamental structure. This exceptional range of isomorphism suggests that these salts may act as ion-exchange media. The salts of 12-molybdophosphoric acid are stable only in acidic solutions, and AMP, which is an insoluble yellow solid under these conditions, provides a good starting material for base exchange investigations.

THISTLETHWAITE[2] noted two points in this connection when he precipitated AMP under the given conditions. Firstly, he found that the precipitates contained only five-sixths of the theoretical amount of ammonium; and secondly, when washed with an acidified solution of potassium nitrate, the precipitates were left with about one-third of their theoretical ammonium content. These results, together with the fact that there was a gain in weight on washing with the potassium solution, suggested that base exchange was occurring, the ammonium ions being replaced by potassium. THISTLETHWAITE was unable to give direct proof of the presence of potassium in the precipitates because expeditious means were not then available for the determination of the small concentrations present.

Whilst preparing precipitates of AMP by THISTLETHWAITE's method and analysing them for ammonium and molybdenum, his results were confirmed. Base exchange studies were undertaken using all the group 1A and other selected cations. Some of the results obtained are summarized below.

Base exchange, unless otherwise stated, was carried out by treating precipitates of AMP for varying periods with acidified solutions (0·08 M in NHO_3) containing an excess of the particular cation as the nitrate (0·1 M to M) and finally with two washes of nitric acid (0·16 M) to remove excess adherent cations. The resulting products, all of which were yellow and insoluble under the given conditions, and in some cases the remaining exchange solutions, were analysed as follows:—

(i) *AMP prepared by* THISTLETHWAITE's *method*

Percentage	*Found*	*Theory*
Mo	60·8–61·7	61·35
(NH_4)	2·26–2·32	2·88
Mo/(NH_4) moles	5·02	4·00
Mols (NH_4)/mol AMP	2·35–2·41	3·00

(ii) *After exchange with potassium ions*

(a) Percentage Mo	59·8–60·1
Percentage (NH_4)	1·26
Mo/(NH_4) moles	8·91–9·02
*Mols of (NH_4) found per mol of AMP	1·35
Mols of K found per mol of AMP	1·05–1·28

The percentage of Mo is slightly lower than for the unexchanged AMP, which is consistent with the fact that heavier potassium ions have been introduced into the molecule. Base exchange has been confirmed, about one mole of ammonium having been replaced by potassium.

*Assuming that the AMP has a molecular weight of approximately 1880.

[1] G. P. BAXTER and R. C. GRIFFIN *Amer. chem. J.* **34**, 204 (1905).
[2] W. P. THISTLETHWAITE *Analyst* **72**, 531 (1947).
[3] I. LINDQVIST *Nova Acta Reg. Sci. Upsal.* **15**, (iv) No. 1 (1950).
[4] J. W. ILLINGWORTH and J. F. KEGGIN *J. chem. Soc.* 575 (1935).

(b) The exchange in this case was carried out using neutral solutions of potassium nitrate followed by two washes with water only.

Mols of (NH_4) found (per mol of AMP)	1·25–1·35
Mols of K found (per mol of AMP)	1·50–1·60
Mols of (NH_4) found in washings after exchange (per mol of AMP)	0·95–1·05

Analysis of the exchange solution shows that one mole of ammonium has been removed from the AMP, whilst 1·5 to 1·6 moles of potassium have been introduced into it. The total of ammonium found in the exchanged material and washings adds up to the amount in the original AMP. The total number of moles of ammonium and potassium found in the exchanged material very nearly adds up to the three theoretically possible. These results confirm THISTLETHWAITE's suggestion that the AMP precipitated under the given conditions is an acid salt containing only five-sixths of the theoretical amount of ammonium. Evidently potassium can replace both hydrogen and ammonium in this salt.

(iii) *After exchange with rubidium and caesium ions*

	Rubidium	*Caesium*
*Mols of (NH_4) found + (per mol of AMP)	0·85–0·95	1·10–1·20
Mols of Rb and Cs found (per mol of AMP)	1·13–1·22	0·99–1·09

*Still assuming a molecular weight of 1880. (This figure will now be low because heavier Rb and Cs ions have been introduced into the molecule.)

These results show a base exchange effect of similar magnitude to that found with potassium and confirm NYDAHL's reported findings.

(iv) *After exchange with thallous ions*

Mols of Tl found (per mol of AMP)	1·95–2·00
Mols of (NH_4) found (per mol of AMP)	1·10–1·15
Mols of (NH_4) found in washings after exchange (per mol of AMP)	1·10–1·20

The ammonium found in the exchanged material and washings totals the amount in the original AMP. It would seem that the Tl^+ ions are taken up more strongly than any of the others investigated, including potassium in neutral solution.

(v) *After exchange with lithium, sodium, calcium, strontium and barium ions*

	Lithium	*Sodium*	*Calcium*	*Strontium*	*Barium*
Mols of metal ion found (per mol of AMP)	0·11	0·07–0·12	0·19–0·21	0·08–0·10	nil*
Mols of (NH_4) found (per mol of AMP)	–	–	–	–	2·08
Mols of (NH_4) found in washings after exchange (per mol of AMP)	0·10–0·20	0·10–0·20	0·10	0·25	0·20

*By weight only

These results, though rather incomplete, show that if base exchange does occur with these ions, it is not of anything approaching the same magnitude as with the heavier group 1A ions and thallous ions.

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ANALYTICAL METHODS

For (NH_4)	semi-micro Kjeldahl type distillation.
Mo	gravimetric as the "oxine".
Li, Na, K, Ca	flame photometrically, using an Eel flame photometer and commercially available filters.
Sr	as above, using the commercial Li filter.
Rb, Cs	as above but using special filters constructed by the authors.
Ba	so far by weight increase only.
Tl	by weight increase and gravimetrically as the iodide and chromate.

CONCLUSION

The results show quantitatively that ammonium 12-molybdophosphate is an efficient base exchanger for potassium, rubidium, caesium and thallous ions, even in acid solutions. The base exchange occurs with the metal ion displacing ammonium and hydrogen ions from the molecule, but it appears that about one mole of ammonium is retained regardless of the conditions.

Further work is being carried out and it is hoped to publish the results in more detail in due course.

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BOOK REVIEW

FARRINGTON DANIELS, JOSEPH HOWARD MATTHEWS, JOHN WARREN WILLIAMS, PAUL BENDER and ROBERT A. ALBERTY: **Experimental Physical Chemistry**, 5th Ed. McGraw-Hill, New York, 1956. vi + 482 pp., 8vo., 49s.

THIS book is a very up-to-date and thorough revision of a well-known text. It is the fifth edition of a book which first appeared about twenty-five years ago and which, in its successive editions, has kept pace with the vigorous growth of physicochemical techniques in this period.

Since much of the progress of modern inorganic chemistry depends upon an ability to make full and proper use of the tools of physical chemistry, this is the kind of book which ought to be in the hands of every young inorganic chemist.

If one were starting a new research student on a problem which involved an unfamiliar technique of measurement, one might well tell him to start with this book and work through the appropriate section and the relevant references.

The first sixteen chapters consist of detailed descriptions, with the necessary theoretical background, of some fifty to sixty experiments which can be carried out in an undergraduate laboratory. There is much to choose from here. Some experiments can be carried out with quite simple apparatus: other involve more advanced apparatus and concepts. As the authors point out, in introducing the latter, if students are not given an opportunity to become familiar with a variety of modern developments and new techniques, they will be handicapped in their later practice of chemistry. There is a commendable flexibility in the instructions and "Suggestions for Further Work" for those who wish to have a closer acquaintance with a particular technique.

The second part (ten chapters) of the book embodies some very lucid accounts of the principles of a large number of experimental techniques. This will be of especial use to the research worker.

In the first section experiments are included which involve radiochemical techniques and which involve the exchange of deuterium. Experiments in newly developing fields, such as chromatographic adsorption, differential thermal analysis, and high-vacuum technique, have been introduced in the present edition. Throughout the book adequate references are given to more specialized texts and to the original literature.

The book contains a wealth of excellently presented material and markedly few omissions. Some there must be, dictated by the limitations of space. There is no mention of magneto-chemical techniques, which perhaps are of especial interest to inorganic chemists, and some of which, with modern permanent magnets, are well within the compass of an undergraduate laboratory.

The book is well printed and illustrated and is very readable.

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ERRATUM

J. Inorg. Nucl. Chem. **5**, 213 (1957).

H. A. MAHLMAN and G. K. SCHWEITZER: Radiation-induced nitrate formation from concentrated nitrate solutions.

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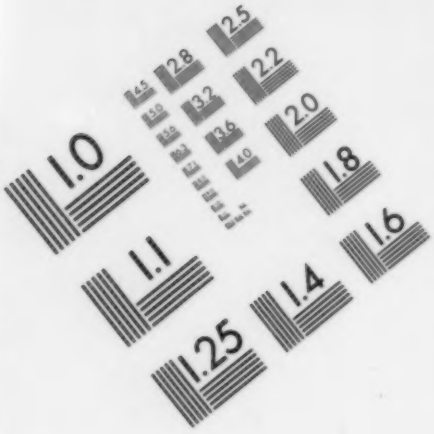

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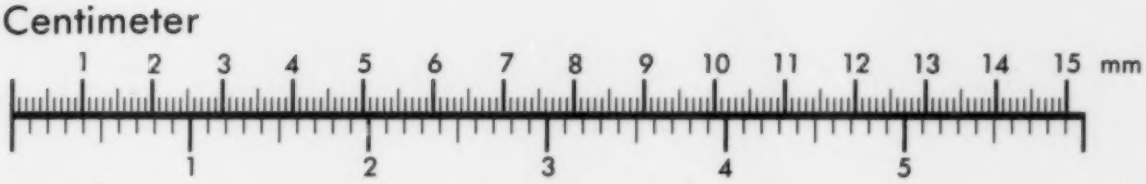

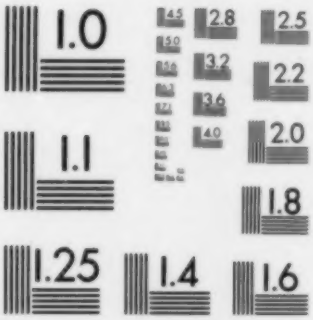

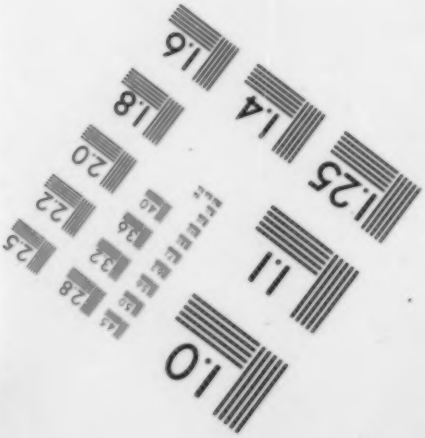

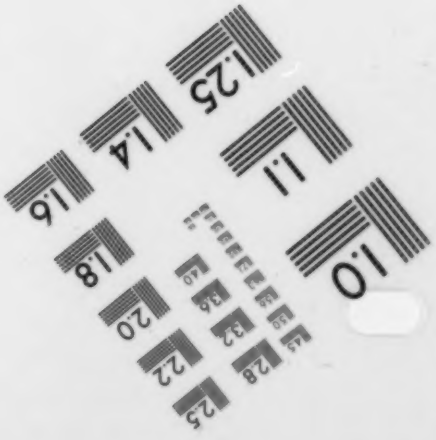

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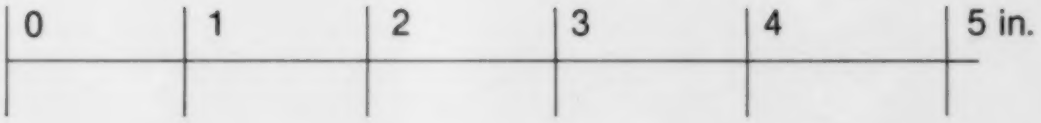

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